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ESR Spectra and Electronic States of 1,10-Phenanthroline Radical Anions

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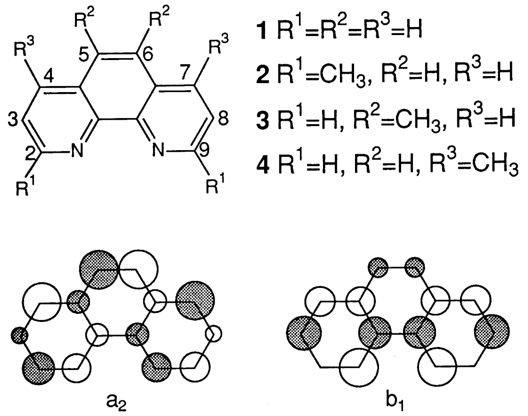
Synopsis. The ESR spectra of the radical anions of 2,9- and 5,6-dimethyl-1,10-phenanthrolines have shown that these radical anions are in the $^2B_1$ state, as is the unsubstituted 1,10-phenanthroline radical anion. MO calculations have indicated that the two lower electronic states of these radical anions, $^2B_1$ and $^2A_2$, lie close to each other, and that the relative stability is largely affected by an interaction with the counter cation.

The bidentate complex ligand, 1,10-phenanthroline (**1**), has two lower unoccupied molecular orbitals, a_2 and b_1, as shown in Fig. 1, which are available to accommodate an additional electron when it is reduced to a radical anion($\mathbf{1}^{-\bullet}$).[1–4] Gooijer et al. have measured the ESR spectra of $\mathbf{1}^{-\bullet}$ and have analyzed them as the $^2A_2$ state.[5] On the other hand, Kaim has examined the electronic state of $\mathbf{1}^{-\bullet}$ by means of ESR measurements and HMO calculations in detail, and has concluded that $\mathbf{1}^{-\bullet}$ is in the $^2B_1$ state.[3] Since the energy levels of the two orbitals are close to each other,[1] the radical anions of the 1,10-phenanthroline derivatives have the possibility of being the $^2A_2$ state due to the influence of substituents, solvents, and counter ions. In this study, the ESR spectra were observed for the radical anions of 2,9- and 5,6-dimethyl-1,10-phenanthrolines ($\mathbf{2}^{-\bullet}$ and $\mathbf{3}^{-\bullet}$) in order to examine their electronic ground states. The stability of each of the electronic states was examined by MO calculations which included the lithium cation as the counter ion.



1 $R^1=R^2=R^3=H$
2 $R^1=CH_3$, $R^2=H$, $R^3=H$
3 $R^1=H$, $R^2=CH_3$, $R^3=H$
4 $R^1=H$, $R^2=H$, $R^3=CH_3$

Fig. 1. Numbering of atoms in 1,10-phenanthrolines and schematic representation of two lower unoccupied molecular orbitals of **1**.

ESR Spectra. The commercially available starting

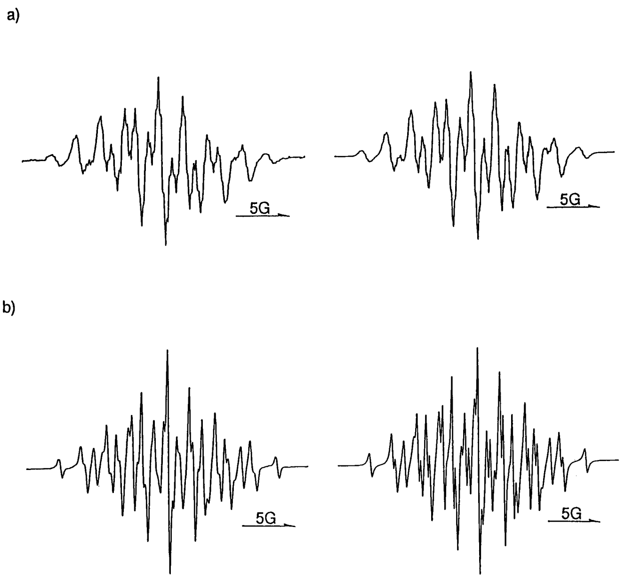


Fig. 2. ESR spectra (left) and simulated spectra (right) for (a) $\mathbf{2}^{-\bullet}$ and (b) $\mathbf{3}^{-\bullet}$ obtained by reduction with potassium in DME at −40 °C.

Table 1. Hyperfine Coupling Constants (mT) of Radical Anions $\mathbf{1}^{-\bullet}$—$\mathbf{4}^{-\bullet}$

Radical	Metal	Solvent	a_N	$a_{H(2,9)}$	$a_{H(3,8)}$	$a_{H(4,7)}$	$a_{H(5,6)}$	a_M
$\mathbf{2}^{-\bullet}$	K	THF	0.266	0.024a)	0.385	0.275	0.043	b)
	K	DME	0.270	0.023a)	0.387	0.273	0.036	b)
	Na	THF	0.272	0.023a)	0.373	0.274	0.051	b)
	Na	DME	0.274	0.027a)	0.374	0.275	0.050	b)
$\mathbf{3}^{-\bullet}$	K	THF	0.283	b)	0.391	0.238	b)a)	b)
	K	DME	0.278	b)	0.393	0.243	b)a)	b)
	Li	THF	0.288	b)	0.360	0.277	b)a)	0.075
	Li	DME	0.285	b)	0.365	0.271	b)a)	0.071
$\mathbf{4}^{-\bullet}$c)	K	THF	0.262	0.054	0.428	0.112a)	0.054	b)
$\mathbf{1}^{-\bullet}$c)	K	THF	0.280	0.041	0.360	0.280	0.041	b)

a) Methyl proton coupling constant. b) Not observed. c) Ref.3.

Table 2. Calculated Total Energies (a.u.) and Relative Energies (kJ mol^{-1}, in Parentheses) of Radical Anions $1^{-\bullet}$—$3^{-\bullet}$

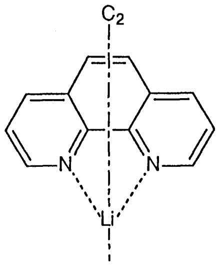
Radical	MNDO		MINI-1//MNDO	
	$^2A_2$ state	$^2B_1$ state	$^2A_2$ state	$^2B_1$ state
$1^{-\bullet}$	−75.75895 (0.0)	−75.75520 (9.8)	−563.71057 (0.0)	−563.70091 (25.4)
$2^{-\bullet}$	−87.27394 (0.0)	−87.26718 (17.8)	−641.22386 (0.0)	−641.21971 (10.9)
$3^{-\bullet}$	−87.25259 (0.0)	−87.24395 (22.7)	−641.22164 (0.0)	−641.21170 (26.1)
$1^{-\bullet}$+Li$^+$	−76.00271 (17.7)	−76.00943 (0.0)	−571.15208 (12.1)	−571.15669 (0.0)
$2^{-\bullet}$+Li$^+$	−87.51589 (8.8)	−87.51924 (0.0)	−648.66591 (29.1)	−648.67701 (0.0)
$3^{-\bullet}$+Li$^+$	−87.49223 (11.0)	−87.49642 (0.0)	−648.66405 (14.8)	−648.66968 (0.0)

compounds, 2,9- and 5,6-dimethyl-1,10-phenanthrolines (**2** and **3**), were sublimed, degassed under vacuum, dissolved in dried and degassed solvent (THF or DME), and then reduced by alkali metals. The ESR spectra were measured with a JEOL JES-FE1XG spectrometer in the temperature range from −70 °C to room temperature. Figures 2a and 2b show that the ESR spectra of $2^{-\bullet}$(a) and $3^{-\bullet}$(b) obtained by reduction with potassium are similar to each other.

The hyperfine coupling (hfc) constants obtained for the radical anions are summarized in Table 1, along with those for the radical anions of 4,7-dimethyl-1,10-phenanthroline and unsubstituted 1,10-phenanthroline($4^{-\bullet}$ and $1^{-\bullet}$) reported by Kaim.[3] The hfc constants of $3^{-\bullet}$ clearly depend on the counter ion; $a_{H(4,7)}$ increases while $a_{H(3,8)}$ decreases by ca. 0.03 mT as the counter ion changes from potassium to lithium. This tendency resembles that observed for the 2,2′-bipyridine radical anion.[6,7] The a_N value of $2^{-\bullet}$ (0.266 mT) is somewhat smaller than that of $1^{-\bullet}$ (0.280 mT); a similar value was obtained for $4^{-\bullet}$ (0.262 mT).[3] In the case of $3^{-\bullet}$ (0.283 mT), where the methyl groups are far from the nitrogen atoms, the substituent effect on the a_N value was not observed.

Although the hfc constants vary with the position of the methyl groups and the counter ion, as mentioned above, they indicate that $2^{-\bullet}$ and $3^{-\bullet}$ are in the $^2B_1$ electronic state. Each of these radical anions has very small a_{CH_3} value, indicating that the π spin densities at the 2,9- and 5,6- positions are very small. Thus, the b_1 orbital corresponds to the SOMO of these radical anions. The radical anions in the $^2A_2$ state are expected to have large a_{CH_3} values; this is not the present case.

MO Calculation. The open-shell RHF method[8] with the MNDO approximation[9] was employed for calculating the relative energies for the $^2A_2$ and $^2B_1$ states. The geometrical parameters of the radical anions were optimized under the restriction of C_{2v} symmetry. The calculated energies are listed in Table 2. Table 2 shows that the $^2A_2$ state is more stable than the $^2B_1$ state for all radical anions. This is contrary to the experimental results. It seems that this discrepancy may come from calculations which do not include the effect of the counter ion. To examine the effect of the counter ion on the electronic states of the radical anions, the following calculations were carried out: The lithium cation was included and its position was optimized on the C_2-axis of the radical anion, the structure of the radical anion being fixed at a geometry which was optimized without a lithium cation. The calculated energies are listed in Table 2. It was found that the $^2B_1$ state becomes more stable than the $^2A_2$ state for all radical anions if the interaction with the lithium cation is included. The b_1 orbital has large coefficients at the nitrogen atoms and interacts with the counter cation preferably to stabilize the $^2B_1$ state.



Scheme.

Ab initio RHF calculations[10] with the MINI-1 basis set[11] were also carried out in order to confirm the above-mentioned results using geometries which were obtained by the MNDO method. They showed the same trend regarding the relative energies between two electronic states as shown in Table 2. That is, the $^2B_1$ state becomes more stable than the $^2A_2$ state if the lithium cation is included.

The experiment has shown that the radical anions of 1,10-phenanthroline and its methyl derivatives have the $^2B_1$ electronic state, while MO calculations have indicated that the counter cation stabilizes the $^2B_1$ state more than the $^2A_2$ state.

References

1) T. Ito, N. Tanaka, I. Hanazaki, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **42**, 702 (1969).
2) W. Kaim, *J. Organomet. Chem.*, **222**, C17 (1981).
3) W. Kaim, *J. Am. Chem. Soc.*, **104**, 3833 (1982).
4) C. C. Phifer and D. R. McMillin, *Inorg. Chem.*, **25**, 1329 (1986).
5) C. Gooijer, N. H. Velthorst, and C. MacLean, *Mol. Phys.*, **24**, 1361 (1972); the hfc constants of $1^{-\bullet}$ obtained are 0.033 (a_N), 0.277 ($a_{H(2,9)}$), and 0.610 mT ($a_{H(5,6)}$).
6) T. Takeshita and N. Hirota, *J. Am. Chem. Soc.*, **93**, 6421 (1971).
7) W. Kaim, *Chem. Ber.*, **114**, 3789 (1981).
8) MNDO calculations were performed using the MOSEMI program package written in our group; O. Kikuchi, K. Morihashi, and T. Kozaki, unpublished.
9) M. J. S. Dewer and W. Thiel, *J. Am. Chem. Soc.*, **99**,

4899, 4907 (1977); the lithium parameters were taken from MNDOC, W. Thiel, *QCPE,* **2** (No. 438), 63 (1982).

10) MINI-1 calculations were performed using the ABINIT program written in our group; O. Kikuchi, T. Nakano, and K. Morihashi, unpublished.

11) H. Tatewaki and S. Huzinaga, *J. Comput. Chem.,* **1**, 205 (1980); Y. Sakai, H. Tatewaki, and S. Huzinaga, *J. Comput. Chem.,* **2**, 100 (1981).