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Conformational Change of Benzoquinone Crown Ether Radical Anions Induced by Complexation with Alkali Metal Cation: An ESR Study

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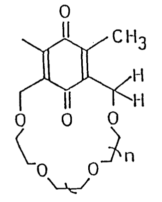
The crowned *p*-benzoquinone anion radicals, **O5**$^-$—**O8**$^-$, were generated either electrochemically or by using a reducing metal, and their ESR spectra were examined in both the absence and presence of the Na^+ or K^+ cation. The hyperfine coupling (hfc) constants of the methylene protons bonded to the quinone ring depend largely on the size of the crown ring; the orientation of the benzoquinone skeleton with respect to the crown ring was analyzed. The metal-free **O5**$^-$ has a fixed conformation in which the benzoquinone ring is nearly perpendicular to the crown ring, while **O8**$^-$ interconverts freely between two equivalent conformations. The critical case is **O6**$^-$; the line-width alternation observed in its ESR spectra was well-analyzed using the two-jump model. Temperature-dependent ESR spectra and MNDO calculations have suggested that **O6**$^-$ undergoes a restricted interconversion between two conformations in which the benzoquinone ring has an orientation similar to that of **O5**$^-$. An activation energy of 10.0 kcal mol^{-1} was determined for this motion. The ESR spectra of the ion-paired **O5**$^-$—**O8**$^-$ anion radicals have suggested that the conformational motion of the anion radicals is fixed by complexation with the Na^+ or K^+ cation. The hfc constants of the methyl protons in the benzoquinone ring increased upon complexation, indirectly confirming the interaction between the carbonyl oxygen of benzoquinone at the crown-ring side and the metal cation.

In the field of host–guest chemistry, studies of molecular switching in macrocyclic polyether systems is of great interest in relation to ion-transport phenomena in biological systems. The crown compounds including redox active functional groups, such as quinone,[1-13] nitrobenzene,[14-17] disulfide,[18] azo moieties,[19] have attracted much attention. Among them, quinone derivatives are especially interesting because they have significant properties due to the ready reversibility of the quinone–semiquinone redox system.

Our previous cyclic voltammetric study has shown that the complexation of crowned quinones, **O5**—**O8**, with alkali metal cations, Li^+, Na^+, or K^+, is enhanced by the reduction of the quinones.[6] Wolf and Cooper showed an ESR spectra which confirmed the interaction between **O6**$^-$ and the Na^+ cation.[7] Bock and Herrmann have shown that **O6**$^-$ forms a 1-to-2 complex with two alkali metal cations.[8] Delgado et al. have reported the ESR spectra of anthraquinone podands and anthraquinone crown ether anion radicals and have shown the interaction between these anion radicals and the alkali metal cation.[10-13] However, there have only been few reports[8,20] concerning the electronic structure and conformational change of the crowned anion radicals induced by interactions with alkali metal cations.



O5: $n = 1$
O6: $n = 2$
O7: $n = 3$
O8: $n = 4$

In this study, the anion radicals of **O5**—**O8**[6] were generated either electrochemically or using a reducing metal, and their ESR spectra were examined both in the absence and presence of a metal cation. From the determined hfc constants and an MNDO[21] calculation of a model anion radical, the conformational change of anion radicals induced by complexation with metal cations is discussed.

Experimental

Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under an Ar atmosphere and stored over 3 Å molecular sieves. The THF was flask-to-flask distilled in a vacuum line immediately prior to use for reduction with an alkali metal. The acetonitrile (MeCN) used for electrochemical reduction was distilled from CaH_2 under an Ar atmosphere. The MeCN was stored without molecular sieves, since they contain Na^+ cations as a component. Tetrabutylammonium perchlorate (TBAP) was twice recrystallized from EtOAc and dried over vaccum pumping at room temperature for 24 h. Alkali metal perchlorate salts, $NaClO_4$ and $KClO_4$ were recrystallized from deionized water and dried over vaccum pumping at 100 °C for 24 h.

The crowned anion radicals were generated by reduction with Na or K metal in THF, and the ESR spectra of ion-paired anion radicals were recorded. The ESR spectra of "metal-free" anion radicals were obtained by the addition of a large excess amount of cryptand 221 to a sample solution prepared with Na metal. The anion radicals were also generated by electrochemical reduction in MeCN using TBAP as a supporting electrolyte. In order to obtain the ESR spectra of the ion-paired anion radicals, 1.0 or 2.0 equivalent of alkali metal perchlorate was used instead of TBAP.

The ESR spectra were recorded on an X-band JEOL JES-FE-1XG spectrometer. The temperature of the samples was controlled by means of a JEOL ES-DVT 1 variable-temperature unit. The microwave frequency was measured with an Advantest TR5212 Microwave Counter and the magnetic feld strength with an Echo Electronics EFM-2000 NMR Field Meter. Field gradients were corrected by using Fremy's salt as a reference compound.

Results

The well-resolved ESR spectra of the metal-free anion radicals and the anion radicals ion-paired with Na^+ or K^+ were obtained for **O5**—**O8**. The hfc constants were determined by simulation, and are summarized in Tables 1 and 2. In the case of the ion-paired **O5**$^-$ generated by reduction with alkali metal, the spectrum changed rapidly and the hfc constants could not be determined. The ESR spectra have the following common features: (1) each spectrum has splitting due to six methyl protons and the methylene protons attached to the quinone ring; (2) the spectra of the metal-free **O6**$^-$ and **O7**$^-$ exhibit a line-width alternation indicating restricted interconversion between conformers; and (3) the Na splitting is observed for **O5**$^-$—**O8**$^-$, while no K splitting is observed.

Reduced O5. Figure 1a shows the ESR spectrum of **O5**$^-$ obtained by reduction with Na metal in THF at 25 °C in the presence of cryptand 221. The ESR spectrum comprises seven main lines arising from the six equivalent methyl protons; each of these lines is further split by the methylene protons attached at the quinone ring. The hfc constants are 2.17 G (6H, $1G=10^{-4}$ T), 0.78 G (2H), and 0.38 G (2H). As was expected, there was no hfc by Na^+ in the presence of the cryptand, and the spectrum of the metal-free **O5**$^-$ was observed. Figure 1b shows the ESR spectra of the metal-free **O5**$^-$ observed by electrochemical reduction. The four methylene protons are equivalent in the MeCN solution. Figure 2 shows the ion-paired **O5**$^-$ observed by electrochemical reduction. The hyperfine coupling of Na was observed, while

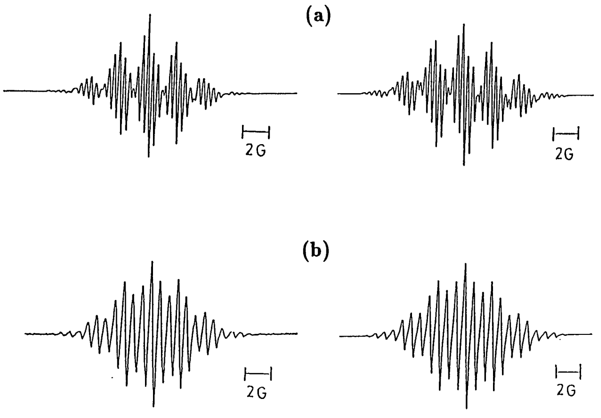


Fig. 1. ESR spectra (left) and corresponding simulated spectra (right) for reduced **O5** obtained (a) by reduction with Na metal in the presence of cryptand 221 and (b) by electrochemical reduction.

Table 1. Observed Proton Hyperfine Coupling Constants (in Gauss) upon Reduction with Alkali Metal in THF at +25°C

Ligand	M^+	$a(CH_3, 6H)$	$a(CH_2)$			a(Na)	LW[a]
O5$^-$	None[b]	2.17	0.78 (2H)		0.38 (2H)	—	0.16
O6$^-$	None[b]	2.11	0.96 (2H)		0.30 (2H)	—	0.14
	Na^+	2.75	0.72 (2H)		—	1.16	0.20
	K^+	2.61	0.72 (2H)		—	—	0.45
O7$^-$	None[b]	2.13		0.64 (4H)		—	0.30
	Na^+	2.80		0.33 (4H)		0.70	0.13
	K^+	2.65		0.36 (4H)		—	0.25
O8$^-$	None[b]	2.16		0.65 (4H)		—	0.25
	Na^+	2.79		0.40 (4H)		0.59	0.16
	K^+	2.63		0.42 (4H)		—	0.20

a) Line width (in Gauss) used for simulation. b) Measured in the presence of cryptand 221.

Table 2. Observed Proton Hyperfine Coupling Constants (in Gauss) upon Electrochemical Reduction in MeCN at +25°C

Ligand	M^+	Equiv	$a(CH_3, 6H)$	$a(CH_2)$			a(Na)	LW[a]
O5$^-$	None	—	2.02		0.65 (4H)		—	0.18
	Na^+	1.0	2.49	0.97 (2H)		—	0.97	0.23
	K^+	1.0	2.25	1.17 (2H)		—	—	0.25
O6$^-$	None	—	2.02	0.97 (2H)		0.25 (2H)	—	0.13
	Na^+	1.0	2.48	0.89 (2H)		—	1.25	0.18
	K^+	1.0	2.41	0.93 (2H)		—	—	0.31
O7$^-$	None	—	2.08	0.98 (2H)		0.26 (2H)	—	0.15
	Na^+	1.0	2.44		0.48 (4H)		0.80	0.24
	K^+	1.0	2.35		0.46 (4H)		—	0.25
O8$^-$	None	—	2.09		0.73 (4H)		—	0.25
	Na^+	2.0[b]	2.95		0.52 (4H)		—	0.20
	K^+	1.0	2.31		0.52 (4H)		—	0.28

a) Line width (in Gauss) used for simulation. b) **O8**$^-$ forms a 1-to-2 complex with Na^+ cation upon electrochemical reduction.

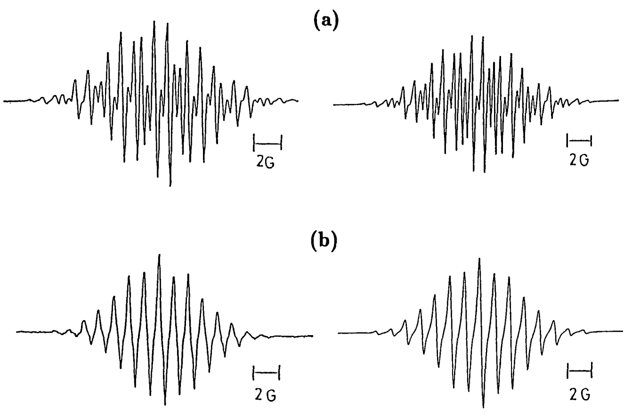


Fig. 2. ESR spectra (left) and simulated spectra (right) for reduced **O5** obtained by electrochemical reduction (a) in the presence of 1.0 equiv of Na^+ and (b) in the presence of 1.0 equiv of K^+.

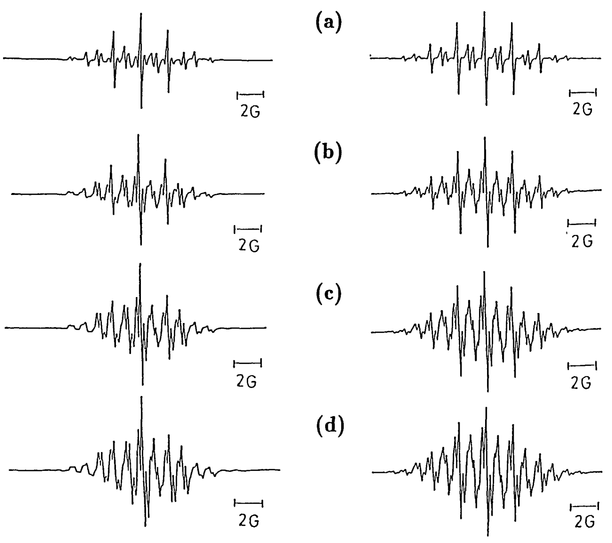


Fig. 3. Temperature-dependent ESR spectra (left) and simulated spectra (right) for metal-free **O6**$^-$ in THF at (a) +25 °C, (b) 0 °C, (c) −20 °C, and (d) −40 °C.

that of K was not resolved.

Reduced O6. Figure 3 shows the temperature dependence of the ESR spectra of the metal-free **O6**$^-$ obtained by reduction with Na in THF in the presence of cryptand 221. The spectra clearly exhibit an alternating line-width effect at room temperature and below, indicating a conformational interconversion of **O6**$^-$. The temperature-dependent spectra were analyzed using a two-jump model between two conformations in which the methylene protons which bonded to the quinone ring were distinguished as being two sets of two equivalent protons. The determined hfc constants are 2.11 G (6H), 0.96 G (2H), and 0.30 G (2H). The rate constant at 25 °C was k=2.5×10^6 s^{-1}. From a plot of log k against 1/T, an activation energy of 10.0 kcal mol^{-1} was determined for the conformational interconversion. Similar hfc constants were obtained for the metal-free **O6**$^-$ generated by electrochemical reduction in MeCN.

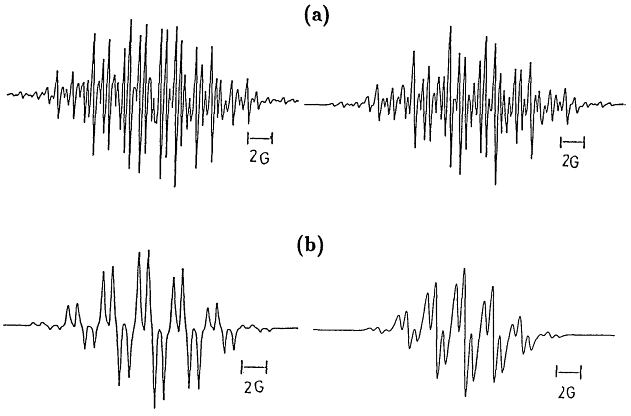


Fig. 4. ESR spectra (left) and simulated spectra (right) for reduced **O6** obtained by reduction with alkali metal (a) in the presence of Na^+ and (b) in the presence of K^+.

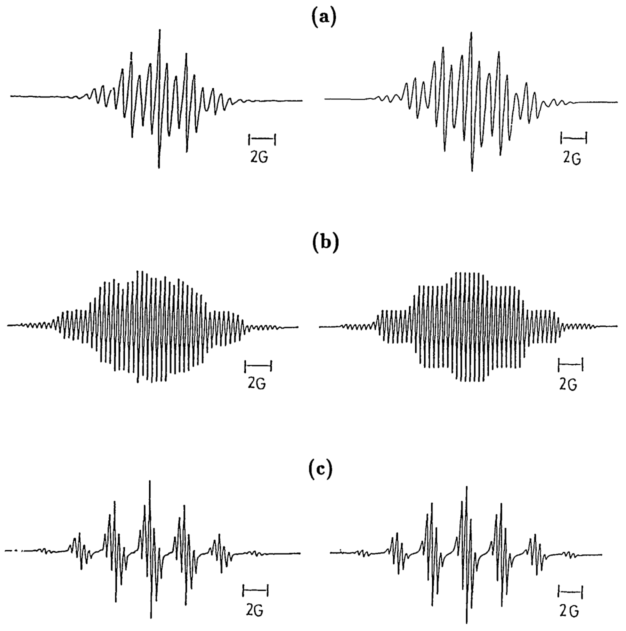


Fig. 5. ESR spectra (left) and simulated spectra (right) for reduced **O7** obtained by reduction with alkali metal (a) in the presence of Na^+ and cryptand 221, (b) in the presence of Na^+ and (c) in the presence of K^+.

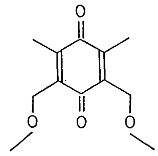
Figure 4 shows the ESR spectra of the ion-paired **O6**$^-$ obtained by reduction with Na or K metal; a splitting of Na was observed. No line-width alternation can be observed in the spectrum, and only one set of methylene protons (2H) has a distinct hfc constant. This characteristic of the ESR spectrum was also observed in the **O6**$^-$–Na^+ or **O6**$^-$–K^+ system obtained by electrochemical reduction. These results suggest that **O6**$^-$ has a conformation in which one of the CH_2 protons lies on the quinone ring plane.

Reduced O7. Figure 5 shows the ESR spectra of **O7**$^-$

observed by reduction with alkali metal. The metal-free **O7**$^-$ spectrum observed by reduction with Na metal has hfc constants of $a(2CH_3)=2.13$ G and $a(4H)=0.64$ G. In the metal-free **O7**$^-$ spectrum obtained by electrochemical reduction, a slight line-width alternation effect was observed; the spectrum was well reproduced by the hfc constants of $a(2CH_3)=2.08$ G, $a(2H)=0.98$ G, and $a(2H)=0.26$ G. These hfc constants of methylene protons indicate that the value of 0.64 G for 4H protons of **O7**$^-$ obtained by reduction with alkali metal is due to an average of two different sets of two protons. In the case of ion-paired **O7**$^-$, four methylene protons have the same hfc constants, irrespective of the method of radical generation.

Reduced O8. All ESR spectra of **O8**$^-$ have no line-width alternation effect, and exhibit the hfc of six equivalent methyl protons and four equivalent methylene protons. Although the hyperfine coupling of Na was observed for **O8**$^-$ ion-paired with Na^+ generated by Na metal, no Na splitting was observed when the radical anion was generated by electrochemical reduction (Fig. 6). In the latter case, 2.0 equivalents of Na^+ are present in the solution and two cations bind with **O8**$^-$; this was confirmed by a previous cyclic voltammetric study.[6]

MNDO Calculation. The orientation of the polyether groups relative to the quinone moiety plays an important role in the energy stabilization of **O5**$^-$—**O8**$^-$. Therefore, the MNDO MO calculations were carried out for the anion radical of a simple model compound, **O3**, in order to examine the conformational energy of **O5**$^-$—**O8**$^-$.



O3

The rotation angle of the CH_2OCH_3 group, ϕ, was measured from the conformation in which the C(methylene)-O(ether) bond lies on the quinone ring plane. Except for the structure of the methyl groups, which was assumed to be tetrahedral with $R_{CH}=1.100$ Å, all geometrical parameters were optimized under the restriction of Cs symmetry for several ϕ values. The open-shell RHF MNDO method[22] was used. The calculated energy profile is shown in Fig. 7. A similar energy profile was also obtained by a UHF MNDO calculation.

A maximum-energy structure was found at $\phi=0°$, where the two C(methylene)-O(ether) bonds are in the quinone ring plane. In such a conformation, the Coulombic repulsion between the ether and carbonyl oxygen atoms becomes maximum. The increase in stabilization in going from $\phi=0°$ to $\phi=90°$ is attributed to a decrease in the Coulombic repulsion; a minimum-energy conformation was found near $\phi=90°$, where the two C(methylene)-O(ether) bonds are perpendicular to the quinone ring plane. The energy difference between the maximum-energy structure ($\phi=0°$) and the minimum-energy one ($\phi=90°$) was calculated to be 12.0 kcal mol^{-1}.

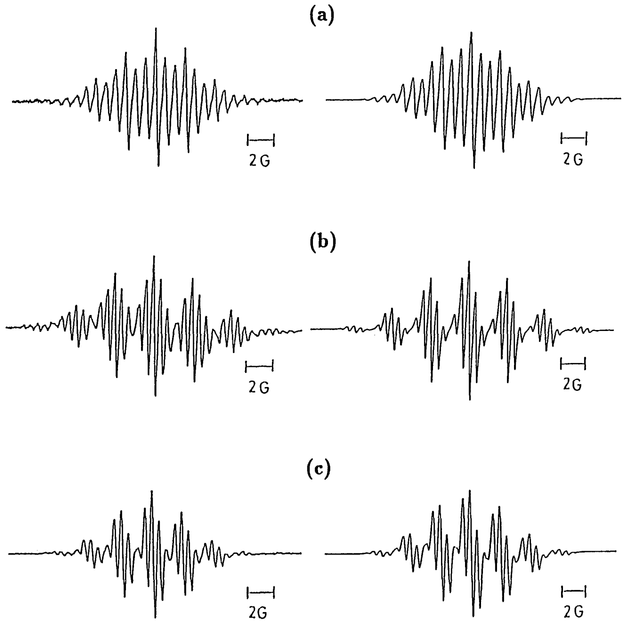


Fig. 6. ESR spectra (left) and simulated spectra (right) for reduced **O8** obtained by electrochemical reduction (a) in the absence of metal catalyst, (b) in the presence of 2 equivalent of Na^+ and (c) in the presence of 1 equivalent of K^+.

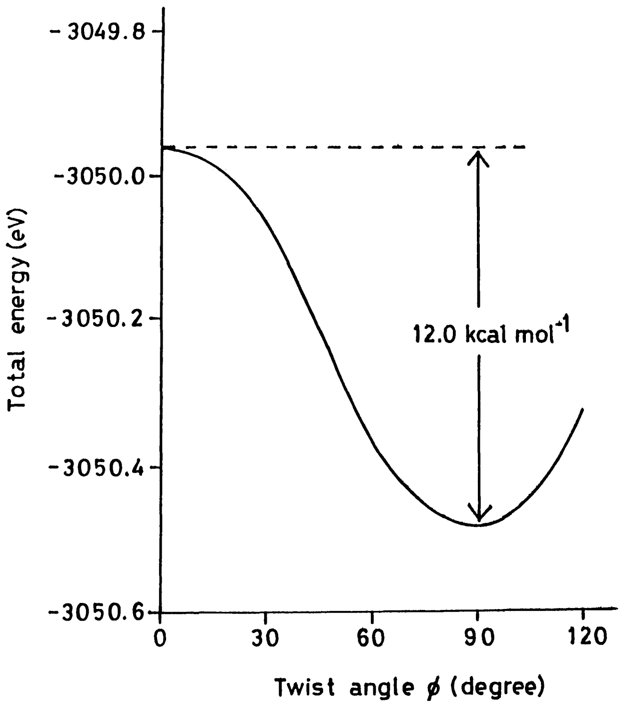


Fig. 7. Energy profile for the rotation of the CH_2OCH_3 groups of the radical anion **O3**$^-$.

Discussion

Metal-Free O6⁻. The present ESR experiment can not determine the conformation of the crown ring skeleton, since the hyperfine coupling due to the methylene protons attached at the quinone ring gives only information concerning the conformational aspects around the C(quinone)–C(methylene) bond. Since the size of the crown ring of **O6⁻** is not large enough to freely undergo a conformational interconversion, the rotation about the C(quinone)–C(methylene) bond is restricted. Because of this steric factor, the four methylene protons attached at the quinone ring are not completely equivalent over the temperature range studied, and the alternating line-width effect was observed.

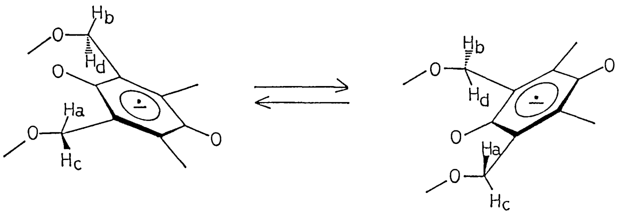
In the two-jump model simulation, four methylene protons attached at the quinone ring were distinguished as being two sets of two equivalent protons: $H_a=H_b$ and $H_c=H_d$ (Scheme 1). We thus assumed an interconversion in which the quinone moiety turns around the C(quinone)–C(methylene) bond. The simulation along this line well reproduced the observed temperature-dependent ESR spectra of the metal-free **O6⁻** (Fig. 3), and the hfc constants listed in Tables 1 and 2 were determined.

The hfc constants of methylene protons depend on the angle, θ, between the C(methylene)–H bond and the $2p_\pi$ orbital of the quinone carbon atom. According to the McConnell–Heller equation,[23]

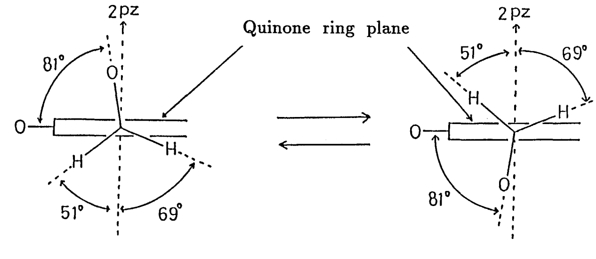
$$a(H_\beta) = B\cos^2\theta,$$

the orientation of the crown ring relative to the quinone moiety can be estimated. From the hfc constant of methyl protons in the duroquinone (2,3,5,6-tetramethyl-*p*-benzoquinone) anion radical, 1.9 G,[24] the empirical parameter, *B*, was estimated to be ca. 3.8 G for the benzoquinone radical anions. From this *B* value and the relative magnitude of the methylene hfc constants observed, 0.96 G and 0.30 G, the conformation of the metal-free **O6⁻** was speculated as **I**.

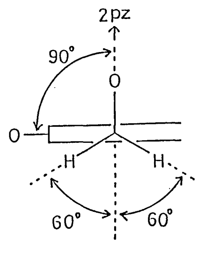
The MNDO calculation of the radical anion of the model compound has shown that the energy-minimum conformation exists near $\phi=90°$. It may thus be said that a conformational interconversion occurs between **I** and **II**. The MNDO calculation has shown that the activation energy of this process is 12.0 kcal mol^{-1}; this value agrees well with the experimentally determined activation energy, $E_A=10.0$ kcal mol^{-1}.



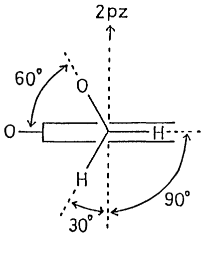
Scheme 1.



I **II**



III



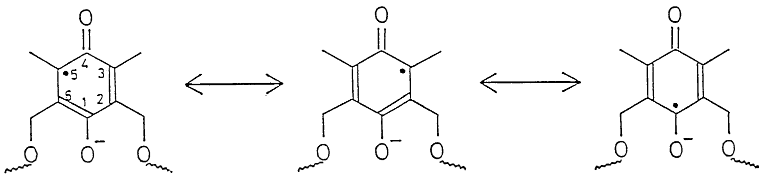
IV

Metal-Free O5⁻. An examination of the CPK model has indicated that the size of the crown ring of the metal-free **O5⁻** is small and that the C(quinone)–C(methylene) bond is hardly allowed to rotate. No alternating line-width effect was observed in the ESR spectrum of the metal-free **O5⁻** and the hfc constants of the methylene protons in THF are similar to those of the metal-free **O6⁻**. These facts suggest that the metal-free **O5⁻** has a fixed conformation which resembles **I** or **II**.

The methylene protons of the metal-free **O5⁻** in MeCN are equivalent. Since the metal-free **O5⁻** has a fixed conformation in THF, it is reasonable to consider that the conformation of the metal-free **O5⁻** is also fixed in MeCN. In this case, the fixed conformer **III** is expected for **O5⁻**.

Metal-Free O7⁻ and O8⁻. The methylene protons of **O7⁻** and **O8⁻** are equivalent in THF. Since metal-free **O6⁻** undergoes a restricted interconversion, the metal-free **O7⁻** and **O8⁻**, which have a larger size crown ring, are expected to undergo interconversion more freely. It is thus natural to consider that the equivalency of methylene protons comes from a rapid exchange between two conformers which resemble **I** and **II**. Actually, the hfc constants of the metal-free **O7⁻** and **O8⁻** are almost the average value of two different hfc constants observed for the metal-free **O6⁻**. In the ESR spectrum of the metal-free **O7⁻** generated by an electrochemical reduction, a line-width alternation was observed; the interconversion is not rapid in this case and the rotation is slightly restricted.

Conformation of Ion-Paired Ligands. For **O5⁻** and **O6⁻** ion-paired with a Na^+ or K^+ cation, only two of four



Scheme 2.

methylene protons exhibit hyperfine coupling. Thus, one of the methylene protons is expected to lie on the quinone ring plane. Therefore, conformation **IV** is suggested for the ion-paired **O5**$^-$ and **O6**$^-$.

In the case of **O7**$^-$ and **O8**$^-$ ion-paired with Na^+ or K^+, four methylene protons were equivalent. As described above, the metal-free **O7**$^-$ shows a restricted conformational interconversion in MeCN. The complexation of **O7**$^-$ with a metal cation is expected to more strongly restrict this interconversion. It is thus reasonable that the equivalency of methylene protons of **O7**$^-$ ion-paired with Na^+ comes from a fixed conformation, like **III**. From the results described above, we believe that all the ligands, **O5**$^-$—**O8**$^-$, have fixed conformations in the presence of alkali metal cations.

hfc Constants of Methyl Protons. As may be seen from Tables 1 and 2, the hfc constant of methyl protons greatly increases (20—30%) when alkali metal cations are present. This may be elucidated on the basis of an interaction between the metal cation and the quinone oxygen atom at the crown ring side. This interaction makes the resonance forms in Scheme 2 more important, and increases the spin densities of the C_1, C_3, and C_5 atoms. This is the reason why the hfc constant of the methyl protons is increased by complexaion with a cation.

It is interesting that the hfc constant of the methyl protons in **O8**$^-$ ion-paired with the Na^+ cation generated by electrochemical reduction is larger than those of other ion pairs. It has been confirmed from a cyclic voltammetric study[6] that **O8**$^-$ forms a 1-to-2 complex with the Na^+ cation. The present large hfc constant suggests that two Na^+ cations are close to the crown ring of **O8**$^-$ and interact with the oxygen atom at the crown ring side, giving a large contribution of the reasonance forms shown in Scheme 2.

Although no K splitting was observed, the hfc constants of the methyl protons increased in the presence of the K^+ cation. This fact suggests that **O5**$^-$—**O8**$^-$ interact with the K^+ cation in the same manner as with the Na^+ cation. It is thus concluded that the semiquinone oxygen atom at the crown ring side interacts with both the Na^+ and K^+ cations and that this interaction influences the spin distribution of the benzosemiquinones anion radicals.

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