Distribution of Unpaired π-Electron in Some Semiquinone Ions

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(Received May 2, 1960)

The hyperfine structure (hfs) of the electron spin resonance (ESR) spectra of free radicals in the dissolved state arises from the interaction between the magnetic moment of the unpaired π-electron and the magnetic moments of the protons and some other magnetic nuclei in the molecule. Based on the spectra of *o*- and *p*-benzosemiquinone ions McConnell has suggested that the magnitude of ring proton splitting constant a_j is approximately proportional to the density of unpaired π-electron ρ_j on the adjacent aromatic carbon atom *j* given by a simple MO treatment, and proposed the relation $a_j=34\rho_j$1). Later he has developed a theoretical study in terms of configurational interaction and concluded that the above-mentioned empirical relation can be used for practical calculation2). This approximation has been applied successfully to the interpretation of hfs of ESR spectra of a number of alternant aromatic hydrocarbon monopositive and mononegative ions3,4).

McConnell has used a set of parameters $\alpha_O=\alpha+\beta$ and $\beta_{CO}=\beta$ in his simple MO treatment of benzosemiquinone ions1). These values have been originally proposed for the oxygen atoms and the carbon-oxygen bonds in neutral quinone molecule5), and the effect of negative charge on the magnitude of these parameters has not been taken into consideration in the treatment of semiquinone ions. Therefore, it seemed to be desirable to find a correct set of parameters for the extension of theoretical work to the semiquinone ions with more complicated molecular structure. The MO treatment with such a set of parameters might be very helpful to the analysis of hfs of ESR spectra of semiquinone ions. In the previous paper the author has attempted to estimate the required parameters based on the frequencies of the C-O stretching vibration in alkali salts of *p*-benzo- and *p*-biphenosemiquinones and obtained a set of $\alpha_O=\alpha+(1/3\sim1/2)\beta$ and $\beta_{CO}=\beta$6). Here we wish to present the results of simple MO treatment with the suggested parameters and compare with the experimental results for several semiquinone ions.

Method of Calculation

The calculations in the present paper were carried out by the simple LCAO MO method. The density of unpaired π-electron at each carbon atom was approximated by the square of the coefficient of its 2*p* function in the singly occupied MO. The coulomb integrals for carbon atoms were assumed to be α, and the exchange integrals were taken as β including that for C-O bonds. The coulomb integral for the oxygen atoms was assumed to be $\alpha+(1/2)\beta$ or $\alpha+(2/3)\beta$. The former value was taken from the previous paper6) and the latter was estimated by the following method. Naphthosemiquinone ion gives a spectrum of three quintets, therefore the density of unpaired π-electron on the aromatic carbon atoms 5 and 5′ is practically equal to that on the carbon atoms 6 and 6′ (see structural formula). The singly occupied MO of this semiquinone ion is antisymmetric. Accordingly, if we assume $\beta_{CO}=\beta$, the magnitude of the coulomb integral for the oxygen atoms $\alpha_O=\alpha+\delta\beta$ can be determined by the system of equations for the coefficient c_j of 2*p* function at carbon atom *j*;

$$
\begin{aligned}
&(y+\delta)c_1+c_3=0\\
&(y-1)c_2+c_3=0\\
&c_1+c_2+yc_3+c_4=0\\
&c_3+(y-1)c_4+c_5=0\\
&c_4+yc_5+c_6=0\\
&c_5+(y-1)c_6=0,
\end{aligned}
$$

where $y=(\alpha-E)/\beta$, and the normalizing condition $\sum c_j^2=1$. If the coefficients of 2*p* function at the carbon atoms 5 and 6 are supposed to be exactly equal to each other, we obtain $\alpha_O=\alpha+(2/3)\beta$. We used $a_j=32\rho_j$ throughout this paper instead of $a_j=34\rho_j$ proposed by McConnell for semiquinone ions simply by the reason that the former seems to fit better with the experimental results. The structural formula and the numbering of oxygen and carbon atoms chosen for convenience are summarized in Fig. 1.

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1) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

2) M. M. McConnell, ibid., **28**, 1188 (1958).

3) E. de Boer and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 4549 (1958).

4) A. Carrington, F. Dravnieks and M. C. R. Symons, *J. Chem. Soc.*, **1959**, 947.

5) M. G. Evans, J. Gergely and J. de Heer, *Trans. Faraday Soc.*, **45**, 312 (1949).

6) Y. Matsunaga, *Can. J. Chem.*, to be published.

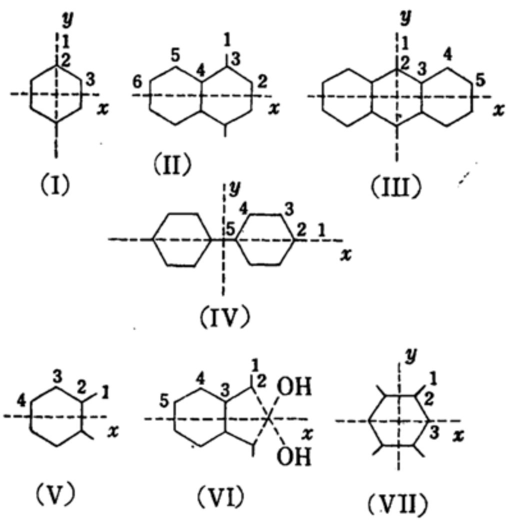

Fig. 1. Structural formula and numbering of oxygen and carbon atoms.

Results and Discussion

***p*-Benzosemiquinone Ion (I).**—This free radical ion has four equivalent protons and gives a predicted quintet with intensity ratios 1 : 4 : 6 : 4 : 1. The splitting constant has been reported as 2.37±0.01 oersteds by Adams, Blois, and Sands⁷⁾. The densities of unpaired π-electron given by a simple MO treatment and the predicted splitting constant are presented in Table I for various values of $\delta=(\alpha_O-\alpha)/\beta$. Since the magnitude of splitting constant depends only slightly on the value of δ, it is hard to tell which value of δ gives the best result.

TABLE I. UNPAIRED ELECTRON DENSITIES (ρ_j) AND SPLITTING CONSTANT (a_3 IN OERSTED) FOR *p*-BENZOSEMIQUINONE ION

δ	ρ_1	ρ_2	ρ_3	a_3
0	0.332	0.032	0.068	2.18
1/2	0.286	0.071	0.071	2.27
2/3	0.264	0.088	0.074	2.37
1	0.221	0.123	0.078	2.50

Naphthosemiquinone Ion (II).—The splitting constants have been reported as 3.22±0.03 oersteds for the ring protons attached to the positions 2 and 2′ and 0.57±0.03 oersteds for those 5, 5′, 6 and 6′. The results of calculation are given in Table II. With a difference of 0.1 oersted it is difficult to distinguish experimentally the splittings due to a_5 and a_6, therefore both of the results obtained assuming $\delta=1/2$ and 2/3 may be considered to be in good agreement with the observed values.

It has been shown that the hf splitting constant for a methyl proton is related to the unpaired π-electron density on the carbon atom, to which the methyl group is attached, by a formula of the same type as for a ring proton⁸,⁹⁾. Besides the proportional constants for these two kinds of protons seem to be nearly the same. As the unpaired electron density in a methyl group is only in the order of 0.01, we may expect the distribution of unpaired π-electron is not much modified by methyl substitution. Therefore, the magnitude of a methyl proton splitting may be close to that of the ring proton attached to the corresponding carbon atom in the unsubstituted free radical ion. The following splitting constants could be assigned for monomethylnaphthosemiquinone ion; 3.2 oersteds for the methyl group attached to the position 2, 2.6 oersteds for the ring proton attached to the position 2′, and 0.6 oersteds for the remaining four ring protons. The spectrum consists of twenty-four lines as shown in Fig. 2. For dimethyl-derivative 2.3 oersteds for the six protons in the methyl groups attached to the positions 2 and 2′ and 0.57 oersteds for the ring protons have been assigned by Vivo¹⁰⁾. Contrary to Vivo's result, an expected quintet with a spacing of

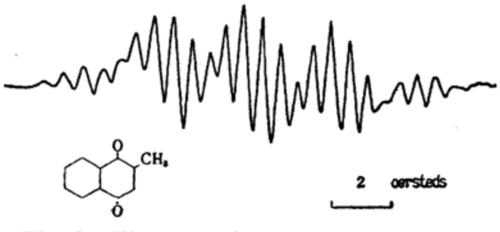

Fig. 2. Electron spin resonance spectrum of monomethylnaphthosemiquinone ion.

TABLE II. UNPAIRED ELECTRON DENSITIES (ρ_j) AND SPLITTING CONSTANTS (a_j IN OERSTED) FOR NAPHTHOSEMIQUINONE ION

δ	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5	ρ_6	a_2	a_5	a_6
0	0.307	0.097	0.040	0.029	0.008	0.019	3.10	0.26	0.61
1/2	0.249	0.099	0.083	0.026	0.019	0.023	3.17	0.61	0.74
2/3	0.225	0.100	0.100	0.025	0.025	0.025	3.20	0.80	0.80
1	0.175	0.103	0.132	0.022	0.039	0.030	3.30	1.25	0.96

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7) M. Adams, M. S. Blois, Jr. and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958).

8) C. B. Chesnut, ibid., **29**, 43 (1958).

9) A. C. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

10) J. L. Vivo, Dissertation, University of Minnesota, 1956.

0.6 oersteds was found in the case of dichloronaphthosemiquinone ion. We may conclude that the ring protons at 5 and 6 are nearly equivalent in all of the examined derivatives.

The semiquinone ion formed on reduction of hydroxynaphthoquinone in alkaline medium has an ionized oxygen atom attached to the position 2. The effect of this substituent is so strong that the distribution of unpaired π-electron in naphthosemiquinone ion is completely changed. The spectrum consists of partially resolved two doublets (1.6 and 1.8 oersteds) instead of two quintets. By comparison with the well-resolved two doublets with 1.5 and 1.9 oersteds given by the semiquinone ion from hydroxychloronaphthoquinone, in which the chlorine atom can be considered inactive to hf splitting, it appears that the observed hfs is entirely due to the interaction between unpaired electron and two protons among four attached to the positions 5, 5′, 6 and 6′ (see Fig. 3).

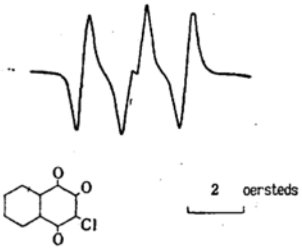

Fig. 3. Electron spin resonance spectrum of the semiquinone ion from hydroxychloronaphthoquinone.

Anthrasemiquinone Ion (III).—This semiquinone ion gives a spectrum of thirteen lines resulting from one set of four equivalent protons and another of four. The splitting constant for one set must be 1.0 oersted and for the other 0.5 oersteds. However, without further information we cannot determine which of the two possible assignments is responsible. The results by simple MO treatment with the proposed parameters suggest that the proton at 5 and its three equivalents give the larger splitting.

TABLE III. UNPAIRED ELECTRON DENSITIES (ρ_j) AND SPLITTING CONSTANTS (a_j IN OERSTED) FOR ANTHRASEMIQUINONE ION

δ	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5	a_4	a_5
0	0.277	0.050	0.046	0.010	0.030	0.32	0.96
1/2	0.214	0.098	0.042	0.021	0.031	0.67	0.99
2/3	0.191	0.115	0.040	0.026	0.031	0.83	0.99
1	0.143	0.143	0.036	0.036	0.036	1.15	1.15

Biphenosemiquinone Ion (IV).—As shown in Table IV, the splitting due to the proton at 3 is expected to be twice or a little more larger than that due to the proton at 4. Unfortunately this free radical ion was found too unstable to be examined by our spectrometer. Tetramethylbiphenosemiquinone ion has four methyl groups attached to the position 3 and its equivalents and gives a spectrum of twenty-one lines with a spacing of 0.78 oersteds[11]. This pattern could be explained using the splitting constants 2.34 oersteds for the ring protons and 0.78 oersteds for the methyl protons as well as using 0.78 oersteds for the ring protons and 1.56 oersteds for the methyl protons. The theoretical results given in Table IV are definitely favorable to the latter assignment.

TABLE IV. UNPAIRED ELECTRON DENSITIES (ρ_j) AND SPLITTING CONSTANTS (a_j IN OERSTED) FOR BIPHENOSEMIQUINONE ION

δ	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5	a_3	a_4
0	0.278	0.005	0.067	0.011	0.060	2.14	0.35
1/2	0.227	0.033	0.062	0.023	0.071	1.98	0.74
2/3	0.202	0.045	0.060	0.028	0.077	1.92	0.90
1	0.152	0.072	0.056	0.038	0.088	1.79	1.22

***o*-Benzosemiquinone Ion (V).**—The three triplets observed in the ESR spectrum of this radical ion have been analyzed by Hoskins[12]. The major splitting has been attributed to the protons attached positions 4 and 4′ and the minor one to those at 3 and 3′. The values have been estimated as 3.65±0.04 and 0.95±0.04 oersteds by Adams et al.[7] Both of the splitting constants calculated using $\delta=1/2$ and 2/3 were found in serious disagreement with the experimetnal ones. Since our parameters seemed not applicable to *o*-semiquinone ions, we attempted to estimate a new one which gives a ratio of $c_4^2/c_3^2=4$ in the present case. Although the value thus estimated as high as 1.611 might suggest that a more refined model is required for the MO treatment of *o*-semiquinone ion, it must be noted that the calculated splitting constants are in good agreement with the observed ones. The unpaired π-electron distribution cited in the last line of Table V is taken from Kuboyama's work on *o*-quinones[13]. As we may expect for the reasons discussed above, his results obtained with the following parameters for neutral quinone molecule predict the splitting constants not far from the experimental ones; $\alpha_O=\alpha+1.3\beta$, $\alpha_2=\alpha+0.2\beta$, $\beta_{22'}=0.8\beta$, $\beta_{23}=\beta_{44'}=0.9\beta$, $\alpha_3=\alpha_4=\alpha$ and $\beta_{12}=\beta_{34}=\beta$.

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[11] Y. Matsunaga and C. A. McDowell, *Can. J. Chem.*, to be published.

[12] R. H. Hoskins, *J. Chem. Phys.*, 23, 1975 (1955).

[13] A. Kuboyama, This Bulletin, 32, 1226 (1959).

TABLE V. UNPAIRED ELECTRON DENSITIES (ρ_j) AND SPLITTING CONSTANTS (a_j IN OERSTED) FOR *o*-BENZOSEMIQUINONE ION

δ	ρ_1	ρ_2	ρ_3	ρ_4	a_3	a_4
0	0.295	0.026	0.113	0.067	3.62	2.14
1/2	0.286	0.071	0.071	0.071	2.27	2.27
2/3	0.272	0.090	0.062	0.076	1.98	2.43
1	0.234	0.128	0.049	0.089	1.57	2.85
1.611	0.155	0.192	0.031	0.123	0.99	3.94
Kuboyama*	0.191	0.176	0.032	0.101	1.02	3.23

* See Ref. 13.

Semiquinone Ion from Ninhydrin (VI). — Adams et al. have observed that ninhydrin on reduction gives a spectrum of three triplets due to the two pairs of equivalent protons on the aromatic ring, and estimated the splitting constants to be 1.95±0.04 and 1.59±0.04 oersteds(7). The conjugated system of this radical ion was considered to be similar to that of *o*-divinylbenzene and examined by the simple MO method changing the magnitude of δ. The results suggest that the larger splitting is attributed to the protons attached to the positions 5 and 5', and the value of δ close to 1.6 is again required for quantitative agreement with the experimental results.

TABLE VI. UNPAIRED ELECTRON DENSITIES (ρ_j) AND SPLITTING CONSTANTS (a_j IN OERSTED) FOR THE SEMIQUINONE ION FROM NINHYDRIN

δ	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5	a_4	a_5
0	0.232	0.071	0.111	0.014	0.071	0.45	2.27
1/2	0.185	0.132	0.093	0.027	0.063	0.86	2.02
2/3	0.167	0.152	0.089	0.031	0.061	0.99	1.95
1	0.132	0.186	0.080	0.041	0.061	1.31	1.95
1.6	0.084	0.231	0.069	0.055	0.061	1.76	1.95

Semiquinone Ion from Dihydroxy-*p*-benzoquinone (VII). — It has been found that the ring proton splitting changes from 1.83 oersteds in dimethyl-*p*-benzosemiquinone ion to 0.30 oersteds in dimethoxy-derivative(11). This considerable decrease suggests the localization of unpaired π-electron on the oxygen atoms in the methoxyl groups. We extended here our measurements to the highly symmetric semiquinone ion formed on reduction of dihydroxy-*p*-benzoquinone. Although we do not know the correct value of δ for this triply charged semiquinone ion, the value must be in the range from −1 for negatively charged oxygen to +1 for the oxygen atom in carbonyl group(14). The singly occupied level predicted by a simple MO treatment for this semiquinone ion is antisymmetric with respect to the *x*-plane. Therefore, no unpaired π-electron density is found on the carbon atoms to which the ring protons are attached and we may expect no hfs in the ESR spectrum of the present radical ion. The small splitting due to the ring protons observed in the case of dimethoxy-*p*-benzosemiquinone ion may be correlated with the difference between the electronegativities for two kinds of oxygen atoms.

Contrary to the expectation, on reduction with sodium dithionate dihydroxy-*p*-benzoquinone dissolved in a mixture of pyridine, ethylene glycol, and 2 N pottasium hydroxide (1:2:1 by volume) shows a triplet with a spacing of 0.78 oersteds. If we substitute the two ring protons with chlorine or bromine atoms, the semiquinone ion gives an expected single line spectrum. Apparently there is the ring proton splitting in the ESR spectrum of the radical ion formed by reduction of dihydroxy-*p*-benzoquinone. The unpaired π-electron density on the adjacent carbon atoms must be as high as 0.02. Therefore, we may conclude that a single configuration MO treatment does give neither the correct symmetyr of energy level nor the correct distribution of unpaired π-electron for the present radical. A similalr disagreement as to the symmetry of energy level has been reported by de Boer and Weissman in the case of pyrene negative ion(3).

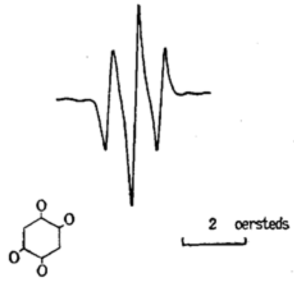

Fig. 4. Electron spin resonance spectrum of the semiquinone ion from dihydroxy-*p*-benzoquinone.

Summary

The distribution of unpaired π-electron was calculated by the simple MO method using the proposed parameters $\alpha_O = \alpha + (1/2)\beta$ and $\alpha + (2/3)\beta$ for six semiquinone ions. The calculated splitting constants for the ring protons in *p*-benzo- and naphtho-semiquinone ions were found in good agreement with the experimental ones and the MO treatment with the proposed parameters seemed to be very helpful to the analysis of the hfs of ESR spectra of anthra- and bipheno-semiquinone ions. In the case of *o*-semiquinone ion, a much higher value of α_O was required to obtain quantitative agreement. The assignment of splitting constants was

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14) H. H. Jaffe, *J. Am. Chem. Soc.*, 77, 4448 (1955).

attempted for the semiquinone ion from ninhydrin. It was found that the simple MO method fails to predict the symmetry of the singly occupied MO in the semiquinone ion formed on reduction of dihydroxy-*p*-benzoquinone. In addition the ESR spectra of the semiquinone ions from methyl- and hydroxy-naphthoquinones etc. were described.

The spectra quoted in this paper were obtained at the University of British Columbia during the tenure of a National Research Council of Canada Postdoctorate Fellowship. The author wishes to express his sincere thanks to Professor C. A. McDowell for his generous keep and hospitality.

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