

## Semi-empirical SCF Calculations of the Spin Distributions in the *p*- and *o*-Benzosemiquinone Anion Radicals

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Recently, the semi-empirical open shell SCF method has been applied to the electronic spectra of aromatic radicals containing hetero-atoms with good agreement with experiments.<sup>1)</sup> In this note the spin distributions are calculated by the open shell SCF procedure of Longuet-Higgins and Pople<sup>2)</sup> with configuration interaction and the unrestricted Hartree-Fock method<sup>3,4)</sup> for *p*- and *o*-benzosemiquinone anions, and the calculated spin densities are compared with the experimental ones estimated from ESR spectra. The semiquinone anions are simple hetero-atom free radicals good for applying the above calculation methods.

### Calculation Procedure

The ASMO for the doublet ground configuration, is described by

1) A. Ishitani and S. Nagakura, *Theoret. chim. Acta (Berl.)* **4**, 236 (1966).

2) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc.*, **68**, 591 (1955).

3) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).

4) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).

$${}^2\Psi_g = |\phi_1\bar{\phi}_1\cdots\phi_{m-1}\bar{\phi}_{m-1}\phi_m| \quad (1)$$

and the excited configurations considered are of the following four types,

$$\left. \begin{aligned} {}^2\Psi_{m\rightarrow k} &= |\phi_1\bar{\phi}_1\cdots\phi_{m-1}\bar{\phi}_{m-1}\phi_k| \\ {}^2\Psi_{i\rightarrow m} &= |\phi_1\bar{\phi}_1\cdots\phi_i\bar{\phi}_m\cdots\phi_{m-1}\bar{\phi}_{m-1}\phi_m| \\ {}^2\Psi_{i\rightarrow k}(\text{I}) &= \frac{1}{\sqrt{2}}(|\phi_1\bar{\phi}_1\cdots\phi_i\bar{\phi}_k\cdots\phi_{m-1}\bar{\phi}_{m-1}\phi_m| \\ &\quad + |\phi_1\bar{\phi}_1\cdots\phi_k\bar{\phi}_i\cdots\phi_{m-1}\bar{\phi}_{m-1}\phi_m|) \\ {}^2\Psi_{i\rightarrow k}(\text{II}) &= \frac{1}{\sqrt{6}}(|\phi_1\bar{\phi}_1\cdots\phi_i\bar{\phi}_k\cdots\phi_{m-1}\bar{\phi}_{m-1}\phi_m| \\ &\quad - |\phi_1\bar{\phi}_1\cdots\phi_k\bar{\phi}_i\cdots\phi_{m-1}\bar{\phi}_{m-1}\phi_m| \\ &\quad - 2|\phi_1\bar{\phi}_1\cdots\phi_i\phi_k\cdots\phi_{m-1}\bar{\phi}_{m-1}\phi_m|) \end{aligned} \right\} \quad (2)$$

where  $\phi_i$ 's are the open shell LCAO SCF MO's and are evaluated by the approximate method of Longuet-Higgins and Pople.<sup>2)</sup> The electronic ground state function,  ${}^2\Phi_g$  is obtained approximately by a linear combination of doublet functions given by Eqs. (1) and (2),

$${}^2\Phi_g = \sum A_i {}^2\Psi_i \quad (3)$$

The spin densities at the various atoms of the  $\pi$ -electronic system are derived from the integral

$$\rho_r = S_z^{-1} \langle \Phi_0 | \sum_{k=1}^{2m-1} S_z(k) A_r(k) | \Phi_0 \rangle \quad (4)$$

In the unrestricted Hartree-Fock method, the following two sets of LCAO SCF MO's are calculated by the method of Brickstock and Pople.<sup>4)</sup>

$$\psi_i^\alpha = \sum_r C_{ir}^\alpha \chi_r; \quad \psi_i^\beta = \sum_r C_{ir}^\beta \chi_r \quad (5)$$

The bond-order matrices, **P** and **Q**, are defined for electrons of spin  $\alpha$  and  $\beta$  as in the following,<sup>5)</sup>

$$P_{rs} = \sum_{i=1}^m C_{ir}^\alpha C_{is}^\alpha; \quad Q_{rs} = \sum_{i=1}^{m-1} C_{ir}^\beta C_{is}^\beta \quad (6)$$

The  $\pi$ -electron spin density at the atom  $r$  is given by

$$\rho_r = P_{rr} - Q_{rr} \quad (7)$$

Amos and Synder<sup>6)</sup> removed the quartet component from the unrestricted Hartree-Fock single-determinant wave function, and from their improved expression, the spin density is calculated by

$$\rho_r = J_{rr} - K_{rr} \quad (8)$$

where the matrices **J** and **K** are expressed by matrices **P** and **Q**.<sup>6)</sup>

One-center atomic orbital integrals are evaluated from the appropriate valence state ionization potential and the electron affinity of the each atom.

Two-center integrals are calculated for larger distances ( $r \geq 2.8$  Å) from theoretical formula<sup>7)</sup> and for smaller distances from the following formula,

$$\gamma_{rs} = ar^2 + br + \frac{1}{2} (\gamma_{rr} + \gamma_{ss}) \quad (9)$$

Core Coulomb integrals are calculated according to the Pariser-Parr approximation<sup>8)</sup> but neglecting penetration integrals. Core resonance integrals are obtained from the Kon's equations.<sup>9)</sup> The electron repulsion integrals, the core Coulomb integrals, the valence state ionization potentials and the electron affinities described above are functions of effective nuclear charges<sup>10,11)</sup> determined from electron densities obtained by each iteration. The structure and the numbering of

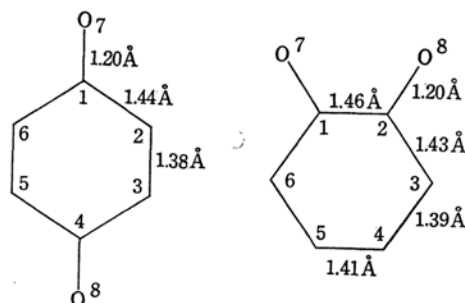


Fig. 1. The structures of *p*- and *o*-benzosemiquinone anions.

TABLE 1. THE CALCULATED AND EXPERIMENTAL<sup>12)</sup> SPIN DENSITY DISTRIBUTIONS IN THE *p*- AND *o*-BENZOSEMIQUINONE ANIONS

Position	Exp.§ <sup>1</sup>	Calc.§ <sup>2</sup>			
		I	II	III	IV
<i>p</i> -Benzosemiquinone					
1	—	0.0937	0.0429	−0.0055	0.0606
2	0.088	0.1112	0.0775	0.0813	0.0900
7	—	0.1840	0.3022	0.3429	0.2594
<i>o</i> -Benzosemiquinone					
1	—	0.0690	0.0152	−0.0389	0.0356
3	0.035	0.1647	0.1547	0.1872	0.1594
4	0.135	0.1036	0.0521	0.0338	0.0655
7	—	0.1672	0.2780	0.3178	0.2395

§1 The value obtained from the equation  $a_{C-H} = 27\rho_C$ ; M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 1350 (1965).

§2 The values calculated by the following methods;

- I) The open shell SCF method of Longuet-Higgins and Pople.
- II) The same method as I with CI.
- III) The unrestricted SCF method using Eq. (7).
- IV) The same method as III using Eq. (8).

5) A. T. Amos and G. G. Hall, *Proc. Roy. Soc. (London)*, **A263**, 483 (1961).

6) A. T. Amos and L. C. Synder, *J. Chem. Phys.*, **41**, 1773 (1964).

7) R. G. Parr, *ibid.*, **33**, 1184 (1960).

8) R. Pariser and R. G. Parr, *ibid.*, **21**, 466 (1953).

9) H. Kon, *This Bulletin*, **28**, 276 (1955).

10) R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958).

11) O. Matsuoka and Y. I'Haya, *Mol. Phys.*, **8**, 455 (1964).

the position in *p*- and *o*-benzosemiquinone anions are shown in Fig. 1.\*<sup>1</sup>

### Results and Discussion

The spin densities calculated by the methods of I, II, III, and IV, and the observed ones<sup>12)</sup> for the *p*- and *o*-benzosemiquinone are tabulated in Table 1.

For the *p*-benzosemiquinone, the calculated spin density at the position 2 is almost satisfactory to explain the ESR splitting constant of the proton at the same position. From these results, the methods II and IV have given better agreement with experiment, and from the theoretical point of view, the spin distribution calculated with configuration interaction (II) and annihilation (IV) should be satisfactory.

For the *o*-benzosemiquinone, the calculated spin density at the position 4 is less than the spin density at the position 3 in contrast with the experimental results.<sup>12)</sup> A similar incorrect result has been obtained for the benzyl radical by the unrestricted Hartree-Fock calculation method<sup>13)</sup>;

the calculated para proton splitting is less than the ortho one (the experimental values were 6.3 gauss ( $a_p$ ) and 5.1 gauss ( $a_o$ )<sup>14)</sup>). The same tendency has been obtained for the phenoxy radical. From these results, it is shown that there is a tendency to make the spin density at ortho position larger than at para position for free radicals of odd alternant benzene derivatives when the calculation taking account of configuration interaction or the calculation by the unrestricted method are carried out.

The spin distribution of *o*-benzosemiquinone was evaluated by McLachlan's method<sup>15)</sup> using the HMO parameters appropriate to simulate the SCF MO's for *o*-benzoquinone.<sup>16)</sup> The results obtained had the same tendency as those shown in Table 1.\*<sup>2</sup>

All numerical calculations were carried out by the HIPAC-103 digital computer in Tokyo Kyoiku University.

\*<sup>1</sup> In order to determine the C-C bond length, the bond orders were obtained from the calculated SCF MO's assuming that the initial C-C bond length was 1.39Å. The C-O bond length was assumed to be 1.20Å. Y. Harada, *Mol. Phys.*, **8**, 273 (1964).

<sup>12)</sup> M. Adams, M. S. Blois, Jr., and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958).

\*<sup>2</sup> By the proper choice of Coulomb and resonance integrals, the agreement of calculated spin densities with experimental ones have been obtained. G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 1333 (1961).  
<sup>13)</sup> L. C. Synder and A. T. Amos, *ibid.*, **42**, 3670 (1965).

<sup>14)</sup> W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, **1964**, 4857.

<sup>15)</sup> A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

<sup>16)</sup> A. Kuboyama and K. Wada, *This Bulletin*, **38**, 1709 (1965).