Some Information Derived from the Infrared Spectra of Ion-radical Molecules. The Spin-density Distribution for the *p*-Chloranil Anion Radical[1]

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The spin-density distribution in the *p*-chloranil anion radical was determined by means of the difference in the bond orders of the conjugated systems between *p*-chloranil and its anion radical, which was estimated on the basis of the stretching force constants. It was found that the spin-density distribution calculated by this method was in good agreement with that estimated by means of the molecular orbital calculations or by means of the hyperfine splitting constants in the ESR absorption. In view of these results, it was suggested that the present method might become a new tool for investigating the unpaired electron distributions of ion-radical molecules in general.

The infrared spectrum of an ion radical is known to be appreciably different from that of its neutral molecule.[2,3] In a previous paper,[3] we examined the infrared spectra(650—4000cm^{-1}) of *p*-chloranil and its anion radical.[4] In order to explain the appreciable frequency differences between their corresponding bands, the fundamental frequencies were assigned, and the simple Urey-Bradley force fields were determined for both the neutral and anion radical molecules. Their stretching-force constants for the bonds in the π conjugated systems were related to the bond orders by the use of the formula of Coulson and Longuet-Higgins.[5] The values of the bond orders thus obtained for *p*-chloranil ant its anion radical were in good agreement with those evaluated by the molecular orbital calculation, except for the C=O bond in the anion radical. These results are presented in Table 1. In view of these results, it seems that the difference in the infrared spectra between these two molecules is almost entirely attributable to the difference in their electronic structures caused by an extra electron on the *p*-chloranil anion radical.[3]

TABLE 1. THE VALUES OF THE BOND ORDERS OF THE C–C, C=C, AND C=O BONDS FOR *p*-CHLORANIL AND ITS ANION RADICAL

Bond	*p*-Chloranil		Its anion radical	
	IR[a]	MO[b]	IR[a]	MO[b]
C–C	0.27	0.30	0.37	0.41
C=C	0.87	0.91	0.79	0.81
C=O	0.82	0.85	0.40	0.70

a) The values obtained from the stretching force constants, which were evaluated from the fundamental frequencies observed in the infrared spectra.

b) The values calculated from the molecular orbitals for *p*-benzoquinone. See T. L. Kunii and H. Kuroda; Rep. Compt. Centre, Univ. Tokyo, **1**, 119 (1968).

The purpose of the present paper is to indicate that the difference in the bond orders between *p*-chloranil and its anion radical, which was obtained from their infrared spectra, leads to the spin-density distribution for the *p*-chloranil anion radical. In this respect, it is interesting to compare the results of our calculations with the spin-density distribution derived from the molecular orbital calculations and with that derived from the hyperfine splitting constants in the ESR absorption.

Calculations

It was assumed, to a first approximation, that the coefficients of the atomic orbitals for the molecular orbitals of the *p*-chloranil anion radical were not so different from the respective ones of *p*-chloranil, when an extra electron enters into the lowest vacant orbital of *p*-chloranil.[6] In this case, the difference in the bond orders between *p*-chloranil and its anion radical seems to be caused solely by the extra electron in the half-occupied molecular orbital of the *p*-chloranil anion radical. The effect of chlorine can be taken into account either by treating chlorine as a heteroatom or by treating the carbon atom bonded to chlorine as a heteroatom.[7] As will be explained below, it was

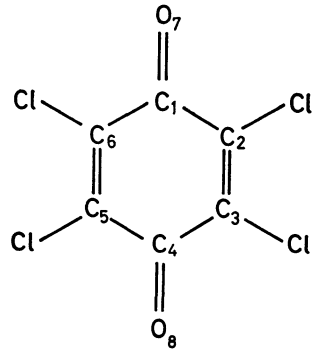

Fig. 1. The structural formula and the numbering of atoms for *p*-chloranil anion radical.

1) This work was presented at the Symposium on Molecular Structure, Tokyo, October, 1970.

2) Y. Matsunaga, *Canad. J. Chem.*, **38**, 1172 (1960); Y. Matsunaga, *Helv. Phys. Acta*, **36**, 800 (1963); Y. Matsunaga, *J. Chem. Phys.*, **41**, 1609 (1964); M. Kinoshita and H. Akamatu, *Nature*, **207**, 291 (1965); J. Stanley, D. Smith, B. Latimer, and J. P. Devlin, *J. Phys. Chem.*, **70**, 2011 (1966).

3) Y. Iida, This Bulletin, **43**, 345 (1970).

4) Actually, the infrared spectrum of the anion radical was measured as that of the crystalline salt with the potassium cation (K$^+$ *p*-Chloranil$^-$).

5) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A193**, 456 (1948).

6) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York and London, 139 (1961).

7) M. Broze, Z. Luz, and B. L. Silver, *J. Chem. Phys.*, **46**, 4891 (1967).

found that the result of our calculations can be well understood by the latter approach. Therefore, let c_i (i=1—8) be the coefficient of the i th atomic orbital in the half-occupied molecular orbital for the p-chloranil anion radical, the structural formula and the numbering of atoms of which are illustrated in Fig. 1. Since, as has already been remarked in a previous paper,[3] the value of the C=O bond order obtained for the anion radical involves some contribution of the self-polarizability, this value must be excluded in our treatment. We use only the values of the bond orders for the homopolar C=C and C–C bonds. Then, from Table 1, as for the C=C bond:

$$c_2c_3 = -0.08 \pm 0.005. \quad (1)$$

The point group for the p-chloranil anion radical belongs to the D_{2h} symmetry. From the symmetry properties, the absolute value of c_2 is equal to that of c_3. If we take c_2 as positive, these relations lead to:

$$c_2 = -c_3 = 0.283 \pm 0.009. \quad (2)$$

As for the C–C bond:

$$c_1c_2 = 0.10 \pm 0.005. \quad (3)$$

Putting the c_2 value into Eq. (3), we obtain:

$$c_1 = 0.354 \pm 0.029. \quad (4)$$

Similarly, since $c_1c_6=c_3c_4=c_1c_2$, and $c_5c_6=c_2c_3$:

$$c_6 = -c_5 = c_2, \quad (5)$$

$$c_4 = -c_1. \quad (6)$$

Although, as has been mentioned above, the values of c_7 and c_8 cannot be obtained directly from Table 1, the following normalization condition allows us to compute these values as:

$$|c_7|^2 = |c_8|^2 = \frac{1}{2}(1.00 - 2|c_1|^2 - 4|c_2|^2)$$

$$= 0.213 \pm 0.010. \quad (7)$$

As we can see from Table 1, the C=O bond order is obviously decreased in the anion radical: $c_1c_7=c_4c_8<0$. Therefore,

$$c_7 = -c_8 = -0.462 \pm 0.010.^{8} \quad (8)$$

Judging from the signs of the coefficients of the atomic orbitals, the symmetry of the half-occupied molecular orbital for the p-chloranil anion radical proves to belong to the b_{3g} irreducible representation; this is in good accordance with that predicted by the electronic-spectrum measurements or the molecular-orbital calculations.[9–11]

The spin density, ρ_i(IR), at the ith atom can, then, be calculated by:[12]

$$\rho_i(\mathrm{IR}) = |c_i|^2. \quad (9)$$

The values of ρ_i(IR) thus obtained for i=1, 2, and 7 are collected in Table 2.

Table 2. The spin density distribution in p-chloranil anion radical

Position, i[a]	ρ_i(IR)[b]	ρ_i(MO)[c]
1	0.127±0.020	0.0918
2	0.080±0.005	0.1025
7	0.213±0.010	0.2031

a) Numbering as in Fig. 1.
b) The values calculated from the difference of the bond orders between p-chloranil and its anion radical, which were derived from the difference of the stretching force constants in their infrared spectra.
c) The values estimated from the molecular orbital calculation by Broze, Luz, and Silver. See Ref. 7.

Discussion

Comparison with the Results of the Molecular-orbital Calculations. In order to account for the ^{17}O hyperfine splitting constant in the ESR absorption, Broze *et al.* have calculated the Hückel molecular orbitals for the p-chloranil anion radical.[7] They assumed the carbon atom bonded to chlorine to be a heteroatom, X, and determined the best-fit value for the ^{17}O hyperfine splitting constant. The optimum parameters for the heteroatom, X, are:

$$\alpha_X = \alpha - 0.012\beta, \quad (10)$$

$$\beta_{CX} = 0.962\beta. \quad (11)$$

As for the oxygen atom:

$$\alpha_O = \alpha + 1.17\beta, \quad (12)$$

$$\beta_{CO} = 1.46\beta. \quad (13)$$

They calculated the spin density, ρ_i(MO), for the p-chloranil anion radical by means of McLachlan's approximation. The values of ρ_i(MO) for i=1,2, and 7 are also collected in Table 2.[7]

As is shown in Table 2, although ρ_1(IR) $-\rho_1$(MO) $\approx$ 0.035, ρ_2(IR) $-\rho_2$(MO) ≈ -0.023, and ρ_7(IR) $-\rho_7$(MO) $\approx$0.010, the agreement between ρ_i(IR) and ρ_i(MO), where i=1, 2, and 7, is fairly good.

Since the α_X and β_{CX} values in Eqs. (10) and (11) are close to those of the corresponding carbon atoms in the p-benzoquinone anion radical, the unpaired-electron distribution in the conjugated system for the p-chloranil anion radical appears to be similar to that for the p-benzoquinone anion radical.

Comparison with the Results on the ESR Hyperfine Splitting Constants. As the p-chloranil anion radical does not include any hydrogen atom, no experimental

8) By the use of the c_1c_7 value and the C=O bond order for p-chloranil, the C=O bond order for the anion radical is corrected to 0.66±0.02. According to the formula of Coulson and Longuet-Higgins,[5] a C=O stretching force constant, K(C=O), in the infrared spectrum is represented by:

$$K(\mathrm{C{=}O}) = \{(1-p(\mathrm{C{=}O}))K_s + p(\mathrm{C{=}O})K_d\} + \left[\left\{\frac{K_sK_d(s-d)}{K_s(1-p(\mathrm{C{=}O}))+K_dp(\mathrm{C{=}O})}\right\}^2 \frac{\pi(\mathrm{COCO})}{2}\right].$$

The notation of this equation and the values of K_s=5.0 md/Å and K_s=10.7 md/Å have already been described in a previous paper.[3] If this equation is applicable to the p-chloranil anion radical, the first term is found to be equal to 8.8 md/Å by the use of p(C=O)=0.66. In this case, since the observed K(C=O) value for the anion radical is 7.3 md/Å, the numerical difference, −1.5 md/Å, may be attributable to the second term involving the self-polarizability. See Ref. 3.

9) Y. Harada, *Mol. Phys.*, **8**, 273 (1964).
10) K. Kimura, H. Yamada, and H. Tsubomura, *J. Chem. Phys.*, **48**, 440 (1968).
11) Y. Iida, This Bulletin, **43**, 2772 (1970).
12) The notation, ρ_i(IR), was used for distinguishing it from the ρ_i(MO) or ρ_i(ESR) to be described in the next section.

result is available for the hyperfine splitting constants except for that due to the ^{17}O of the carbonyl group. Broze *et al.* examined the ESR spectra of the ^{17}O-labeled *p*-chloranil anion radical in various solvents.[7] For example, the ^{17}O hyperfine splitting constant was found to be $a_7^O(\text{obs}) = -8.89 \pm 0.02$ G in a dimethylformamide solution. On the other hand, the theoretical oxygen hyperfine splitting constant, $a_7^O(\text{calc})$, in a carbonyl group can be evaluated by the following equation:[7,13,14]

$$a_7^O(\text{calc}) = Q_{OC}^O \rho_O + Q_{CO}^O \rho_O, \quad (14)$$

where the values of $Q_{OC}^O = -40.7 \pm 5.2$ G and $Q_{CO}^O = -9.5 \pm 6.1$ G were proposed by Broze *et al.*;[7] ρ_O and ρ_C are the spin densities in the $p\pi$ orbitals of the oxygen and the neighbouring carbon atoms respectively. If the values of $\rho_1(\text{IR})$ and $\rho_7(\text{IR})$ are put into Eq. (14), $a_7^O(\text{calc})$ is evaluated to be -10.05 ± 2.48 G; this value is in good agreement with the foregoing experimental value of -8.89 ± 0.02 G.

At present, there appear no experimental data for use in comparing the spin densities on the carbon atoms in the *p*-chloranil anion radical. However, since the unpaired-electron distribution in the conjugated system for the *p*-chloranil anion radical seems to be similar to that for the *p*-benzoquinone anion radical, the values of $\rho_i(\text{IR})$ were compared with the spin densities of the *p*-benzoquinone anion radical as determined from the hyperfine splitting constants.

Das and Fraenkel measured the proton and ^{13}C hyperfine splittings in the ESR spectrum of the *p*-benzoquinone anion radical; they found $a_2^H = -2.395 \pm 0.002$ G and $a_1^C = -2.21 \pm 0.02$ G in the dimethoxyethane solution, while the values were $a_2^H = -2.368 \pm 0.001$ G and $a_1^C = -0.40 \pm 0.04$ G in the C_2H_5OH-H_2O solution.[13] When $i=1$, 2, and 7, the spin densities, $\rho_i(\text{ESR})$, derived from these experimental results were 0.1487, 0.0896, and 0.1721 in the dimethoxyethane solution, while they were 0.1796, 0.0877, and 0.1450 in the C_2H_5OH-H_2O solution respectively.[13] Although there are appreciable differences in the spin densities for the two solvents at the carbonyl carbon and oxygen atoms, we can see that the set of $\rho_i(\text{IR})$, where $i=1$, 2, and 7, is well fitted to that of $\rho_i(\text{ESR})$ in the dimethoxyethane solution. In the case of the C_2H_5OH-H_2O solution, the agreement between $\rho_i(\text{IR})$ and $\rho_i(\text{ESR})$ is not satisfactory, except for that between $\rho_2(\text{IR})$ and $\rho_2(\text{ESR})$.

Concluding Remarks

It has been well established that hyperfine splitting constants in the ESR spectra provide one of the most important means for determining the spin-density distribution of radical molecules.[14] However, this technique involves the following difficulties:

(1) If a radical molecule does not include atoms with a nuclear magnetic moment, no experimental data are available for the hyperfine splitting constants. In practice, when the H, ^{13}C, ^{14}N, or ^{17}O atom is not contained in a radical molecule, the information is, accordingly, quite limited.

(2) If radical molecules exist in an aggregate state, such as in the solid state or in a highly concentrated solution, the hyperfine splittings should be narrowed by intermolecular spin-exchange interaction, which gives only a single exchange-narrowed line.[15] Therefore, the hyperfine splitting constants cannot be obtained in such a situation.

Instead of the use of the hyperfine splitting constants, the spin-density distribution of a radical molecule can be evaluated, in some cases, on the basis of an accurate determination of the *g*-values in the ESR absorption or from the chemical shifts in the NMR spectrum.[14] However, besides these techniques, the present use of the infrared spectra of a neutral molecule and its ion radical constitutes a new approach to this problem. In contrast to the use of hyperfine splitting constants, our method has the following advantages:

(1) A radical molecule need not necessarily include atoms with a nuclear magnetic moment, because the spin densities are derived from the differences in the bond orders.

(2) One can estimate the spin-density distribution for a radical molecule not only in an isolated state, but also in an aggregate state. The latter information seems to be valuable for investigating the intermoleculer interaction of radical molecules. In fact, the values of $\rho_i(\text{IR})$, where $i=1$, 2, and 7, of the *p*-chloranil anion radical are those in the solid state,[3] in which the charge-transfer interaction between *p*-chloranil anion radical molecules has been known to take place by means of the solid-state spectrum.[11] In this respect, one reason for the previously-mentioned small deviation of the $\rho_i(\text{IR})$ values from the $\rho_i(\text{MO})$ or $\rho_i(\text{ESR})$ values, where $i=1$, 2, and 7, may be the difference in the spin-density distributions between the solid state and the isolated state. However, we should keep in mind that, in our treatment, the $\rho_i(\text{IR})$ values include some uncertainties in the course of the derivation of the bond orders from the stretching force constants. This means that more reliable values for the spin densities will be obtained if a more precise estimation of the bond orders and the self-polarizabilities can be made from the stretching force constants.

13) M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 1350 (1965).

14) J. R. Bolton, "Radical Ions," ed. by E. T. Kaiser and L. Kevan, Interscience Publishers, New York, London, and Sydney (1968), p. 1.

15) G. E. Pake, "Paramagnetic Resonance," W. A. Benjamin, New York, 79 (1962).