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Electronic States of *p*-Chloranil and Its Anion-Radical as Revealed by Their Infrared Spectra

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The infrared spectra (650—4000 cm^{-1}) of *p*-chloranil and its anion-radical were measured. Appreciable frequency differences between their corresponding bands were noted. The fundamental frequencies were assigned, and the simple UBFF's were determined for both the neutral and anion-radical molecules. Their stretching force constants for the bonds in the conjugated systems are related to the bond orders. The values of the bond orders thus obtained for *p*-chloranil and 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. In view of these results, it was concluded that the difference in the infrared spectra between these two molecules was almost entirely attributable to the difference in their electronic structures caused by an odd electron on the *p*-chloranil anion-radical. The bond lengths were also estimated on the basis of the bond orders. It was shown that the application of this method might bring valuable knowledge on the molecular and electronic structures of ion-radicals as well as of neutral molecules in general.

It has been noticed that the infrared spectrum of a neutral molecule is appreciably different from that of its ion-radical molecule.[1-5] Obviously, the difference in spectra may be attributed to the difference in their intramolecular force fields. Up to now, however, there has been no attempt to explain the spectrum difference by the use of normal coordinate analysis.

The present paper will describe the infrared spectra of *p*-chloranil and its anion-radical (*i.e.*, the semiquinone ion). The *p*-chloranil molecule is a well-known electron acceptor, and its anion-radical (see Fig. 1) is quite stable. The purpose of this paper is to make a normal coordinate analysis for these molecules and to discuss their molecular and electronic structures on the basis of their intramolecular force fields. In this respect, it is interesting to investigate the effect of an extra electron upon the *p*-chloranil anion-radical.

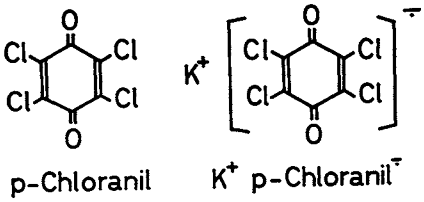

Fig. 1. *p*-Chloranil and its anion-radical salt with potassium cation.

Experimental

Commercially-available *p*-chloranil was purified by recrystallization from benzene and then by sublimation *in vacuo*. Its anion-radical salt with the potassium cation (K^+ *p*-Chloranil$^{\overline{\cdot}}$) was synthesized according to the method of Torrey and Hunter.[6] The infrared spectra of these solid compounds were measured as Nujol mulls in the range from 650 to 4000 cm^{-1} using a HITACHI EPI-S2 infrared spectrophotometer. Alternative

TABLE 1. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) IN THE INFRARED SPECTRA OF *p*-CHLORANIL AND ITS ANION-RADICAL

p-Chloranil			*p*-Chloranil$^{\overline{\cdot}}$		
Obsd	Calcd	Symmetry	Obsd	Calcd	Symmetry
1686(s)	1685	B_{2u}	1524(s)	1520	B_{2u}
1678(sh)					
1571(s)	1569	B_{3u}	1540(s)	1539	B_{3u}
1260(m)	1238	B_{3u}	1176(w)	1288	B_{3u}
1235(m)				(?)	
1115(s)	1116	B_{2u}	1147(s)	1141	B_{2u}
908(m)	916	B_{2u}	918(s)	910	B_{2u}
752(s)	736	B_{3u}	725(s)	736	B_{3u}
715(s)			694(m)		

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1) Y. Matsunaga, *Can. J. Chem.*, **38**, 1172 (1960).

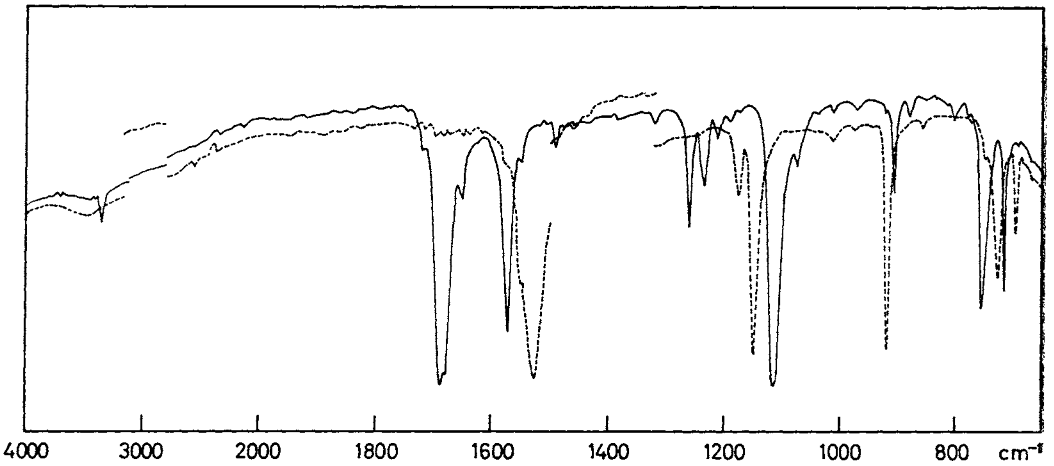
2) Y. Matsunaga, *Helv. Phys. Acta*, **36**, 800 (1963).

3) Y. Matsunaga, *J. Chem. Phys.*, **41**, 1609 (1964).

4) M. Kinoshita and H. Akamatu, *Nature*, **207**, 291 (1965).

5) J. Stanley, D. Smith, B. Latimer and J. P. Devlin, *J. Phys. Chem.*, **70**, 2011 (1966).

6) H. A. Torrey and W. H. Hunter, *J. Amer. Chem. Soc.*, **34**, 702 (1912).



——p-Chloranil, ----K$^+$$p$-Chloranil$^{-\cdot}$

Fig. 2. Infrared spectra of p-chloranil and K$^+$ p-chloranil$^{-\cdot}$.

measurements in the regions where the absorption due to Nujol appears were made using hexachlorobutadiene mulls. The spectra for these compounds are reproduced in Fig. 2. Since the counter cation of the salt is a simple metal cation, the observed spectrum of the salt in the region from 650 to 4000 cm^{-1} should be solely due to that of the anion-radical itself. The values of the absorption peaks observed for p-chloranil and its anion-radical are listed in Table 1.

Normal Coordinate Treatment for In-plane Vibrations

The molecular and crystal structures of p-chloranil were determined by Chu, Jeffrey and Sakurai.[7] Since the molecular and crystal structures of K$^+$ p-Chloranil$^{-\cdot}$ have not yet been ascertained, it was assumed that the molecular structure of the anion-radical was almost identical with that of p-chloranil. This assumption means that the $\boldsymbol{G}$ matrix calculated for p-chloranil was also used for the anion-radical (see below). Since only the intramolecular vibrations are expected to appear in the region from 650 to 4000 cm^{-1}, the vibrational spectra of the crystalline compounds can be approximately treated under the molecular point group D_{2h}. Generally, the effect of crystal fields on vibrational frequencies is small. Therefore, as the first approximation, its contribution to the spectra of p-chloranil and of the anion-radical was ignored in our treatment. Hence, thirty normal modes of vibrations for p-chloranil or its anion-radical were reduced to the symmetry species:

$$\begin{aligned}\Gamma &= 6A_g + 5B_{1g} + 5B_{2u} + 5B_{3u} + 1B_{2g} \\ &+ 3B_{3g} + 2A_u + 3B_{1u}\,, \end{aligned} \tag{1}$$

where the first four are the in-plane vibrations, and the rest, the out-of-plane vibrations.[8] We calculated only the in-plane vibrations, because no out-of-plane vibration is expected to appear in the region now under consideration.

Wilson's $\boldsymbol{GF}$ matrix method was used in this work. The representation of each type of internal coordinate for in-plane fundamental vibrations is given in Fig. 3. A simple Urey-Bradley force field was employed as the potential function. Therefore, four bond-stretching (K(C=O), K(C=C), K(C–C) and K(C–Cl)), five angle-bending (H(O=C–C), H(C–C–Cl), H(C=C–Cl), H(C–C–C), and H(C=C–C)), and five non-bonded repulsion force constants (F(O=C–C), F(C–C–Cl), F(C=C–Cl), F(C–C–C), and F(C=C–C)) were necessary. At

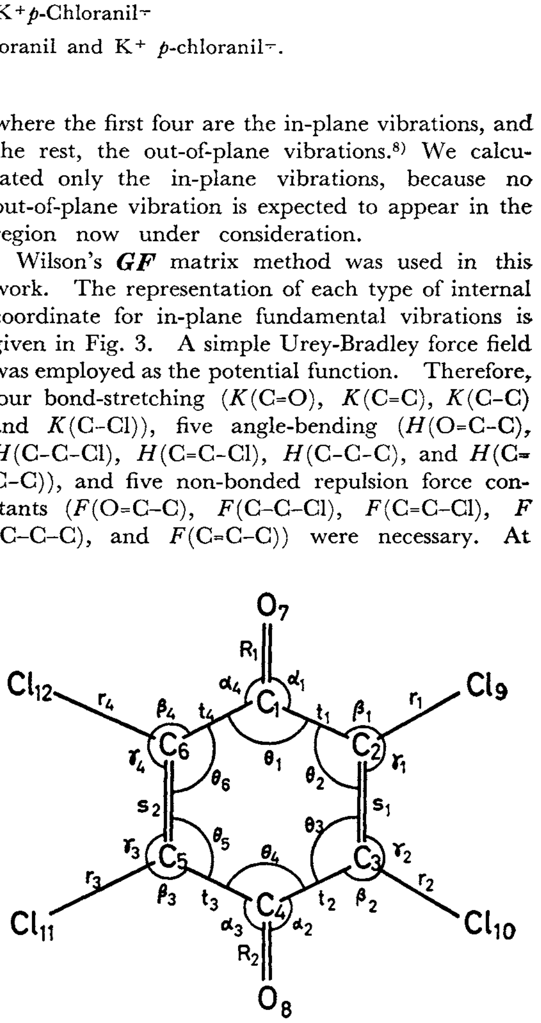


Fig. 3. Internal coordinates for p-chloranil or its anion-radical.

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[7] S. Chu, G. A. Jeffrey and T. Sakurai, *Acta Cryst.*, **15**, 661 (1962).

[8] F. E. Prichard, *Spectrochim. Acta*, **20**, 127 (1964).

TABLE 2. FORCE CONSTANTS FOR *p*-CHLORANIL AND ITS ANION-RADICAL (md/Å)

Force constant	*p*-Chloranil	Its anion-radical
K(C=O)	9.7	7.3
K(C=C)	6.6	6.1
K(C-C)	3.0	3.5
K(C-Cl)	2.67	2.67
H(O=C-C)	0.32	
H(C-C-Cl)	0.08	
H(C=C-Cl)	0.08	
H(C-C-C)	0.229	
H(C-C=C)	0.25	
F(O=C-C)	0.80	
F(C-C-Cl)	0.928	
F(C=C-Cl)	0.928	
F(C-C-C)	0.30	
F(C-C=C)	0.37	

$F' = -0.1F$.

this time, it was assumed that the stretching force constants of *p*-chloranil were different from those of the anion-radical, while the other force constants of *p*-chloranil were almost the same as the corresponding ones of the anion-radical. The initial values of the force constants were transferred from the values for benzene and its chloro-derivatives.[9,10] Refinements of the force constants were then carried out by the trial-and-error method[*1] making use of the Jacobian matrices. The final sets of force constants thus obtained for these molecules are shown in Table 2. In both of these molecules, the calculated values of the fundamental vibrations (see Table 1) agreed well with the observed values, except for the following two points, which remain to be elucidated:

(1) Two absorption peaks were observed, at 752 and 715 cm^{-1} for the neutral molecule or at 725 and 694 cm^{-1} for the anion-radical, while only one fundamental in-plane vibration was expected to appear around this region.[*2] To assign one of them to an out-of-plane vibration is improbable, because such a vibration should appear in the region below 650 cm^{-1}.

(2) The calculated 1288 cm^{-1} band in the anion-radical cannot be assigned to any of the observed bands, presumably because of its weak intensity.

Since a total of 14 force constants were evaluated from an experimental assignment of 6 frequencies, we suspect that these values of the force constants are not the best ones for each of these compounds. However, the stretching force constants are still meaningful, because the observed fundamental frequencies are almost all due to the stretching modes. In the discussion below, we will discuss only the difference in the stretching force constants between *p*-chloranil and its anion-radical.

As is shown in Table 2, appreciable differences in the force constants were found in K(C=C), K(C–C), and K(C=O)—namely, K(C=C) = 6.6 md/Å, K(C–C) = 3.0, and K(C=O) = 9.7 for *p*-chloranil, while K(C=C) = 6.1, K(C–C) = 3.5, and K(C=O) = 7.3 for the anion-radical. From these results, we can see that the stretching force constants for the bonds in the conjugated systems are strongly affected. It is expected that the extra electron on the anion-radical is the essential factor causing the decrease in the values of K(C–C) and K(C–O) and the increase in the value of K(C–C), compared to the values of *p*-chloranil.

Discussion

According to Coulson and Longuet-Higgins,[11] the stretching force constant of a bond (12) in a conjugated system can be expressed by:

$$K(12) = \{(1-p(12))K_s + p(12)K_d\} + \left[\left\{\frac{K_sK_d(s-d)}{K_s(1-p(12))+K_dp(12)}\right\}^2 \frac{\pi(1212)}{2}\right], \qquad (2)$$

where K_s and K_d are the force constants associated with pure single and double bonds respectively; where $p(12)$ is the bond order, and $\pi(1212)$, the self-polarizability, of the bond (12), and where s and d are the bond lengths of pure single and double bonds respectively.

Carbon-Carbon Bonds. In a homopolar carbon-carbon bond, the second term, involving the self-polarizability, may be small.[12] In this case, the stretching force constant, $K(12)$, is predominantly determined by the bond order, $p(12)$. The lower part of Fig. 4 shows the empirical relation of $K(12)$ to $p(12)$, in which several standard points indicated by the open circles are connected smoothly. They were determined on the basis of the values of $K(12)$ and $p(12)$ for the carbon-carbon bonds in the ethylene, benzene, and butadiene molecules.[9,13] Little contribution of $\pi(1212)$ to $K(12)$ is best shown

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9) Y. Kakiuchi, *Nippon Kagaku Zasshi*, **75**, 143 (1954).

10) J. R. Scherer, *Spectrochim. Acta*, **20**, 345 (1964).

[*1] The calculations were carried out on a HITAC 5020E at the Computer Center, The University of Tokyo.

[*2] In *p*-bromanil, the corresponding bands were found at 705 and 650 cm^{-1}, and in its anion-radical, at 684 and 618 cm^{-1}. The bands at 752 and 725 cm^{-1} in *p*-chloranil and its anion-radical shifted to 650 and 618 cm^{-1} in *p*-bromanil and its anion-radical respectively, whereas the speculation of a similar shifts is not adequate to the cases of the other bands. For this reason, the bands at 752 and 725 cm^{-1} in *p*-chloranil and its anion-radical were assigned to the fundamental vibrations of the C-Cl stretching mode.

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

12) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley & Sons, New York and London (1961).

13) K. Ito and T. Shimanouchi, private communication.

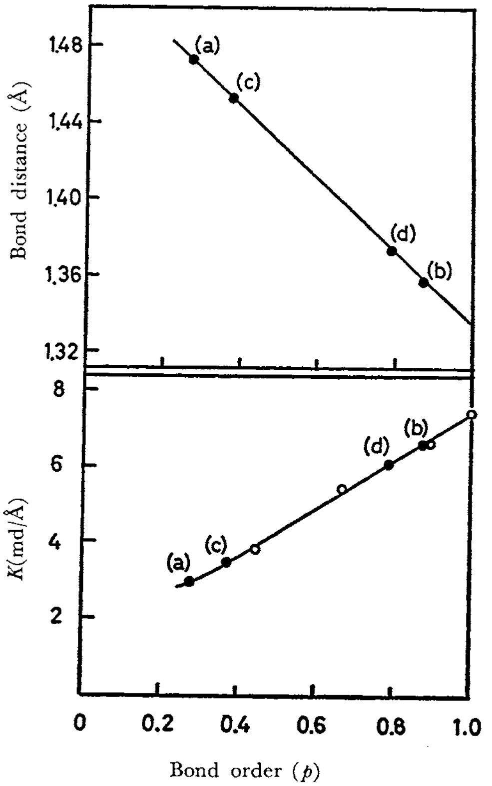

Fig. 4. The lower part illustrates the empirical relation between $K(12)$ and $p(12)$ of a carbon-carbon bond, and the upper part, the relation of $l(12)$ to $p(12)$. (a) and (b) show the values due to C-C and C=C bonds for p-chloranil, and (c) and (d), those for its anion-radical, respectively. Open circles indicate the standard points based on the values of $K(12)$ and $p(12)$ in the ethylene, benzene and butadiene molecules.

by the approximate linearity between the $K(12)$ and $p(12)$ values. We cannot adopt the K(C–C) value of ethane as K_s, because the value of K_s should not be that due to the C_{sp^3}–C_{sp^3} bond of ethane, but that due to the C_{sp^2}–C_{sp^2} bond, with $p(12)=0$.

Table 3. The values of the bond orders of p(C-C), p(C=C) and p(C=O) for p-chloranil and its anion-radical

Bond	p-Chloranil		p-Chloranil$^-$	
	IR[a)]	MO[b)]	IR[a)]	MO[b)]
C-C	0.27	0.20	0.37	0.32
C=C	0.87	0.96	0.79	0.83
C=O	0.82	0.91	0.40	0.79

a) The values obtained from the stretch force constants.

b) The values calculated from the molecular orbitals.

By the use of this empirical formula, we can evaluate the bond orders of the C=C and C–C bonds for p-chloranil and its anion-radical. From the values of K(C=C) and K(C–C) in their infrared spectra, the p(C=C) and p(C–C) values for these molecules were estimated to be as shown in Table 3. It seems that the extra electron on the anion-radical leads to a decrease in p(C=C) of 0.08 and to an increase in p(C–C) of 0.10, compared to the values of the neutral p-chloranil. In order to confirm this result, we further calculated the p(C=C) and p(C–C) values of these molecules by the use of their molecular orbitals. For simplicity, the SCF molecular orbitals of p-benzoquinone were used,[14)] because the electronic state of the π-conjugated system in p-chloranil can be regarded as very similar to that in p-benzoquinone. We also assumed that the extra electron enters into the lowest-vacant orbital of p-benzoquinone. This orbital has the irreducible representation of the symmetry, b_{3g}, where the coefficients of the O_7, C_1, C_2, and C_3 atomic orbitals were assumed to be represented by -0.3564, $+0.3315$, $+0.3627$, and -0.3627 respectively.[14)] With these assumptions, we calculated the values of p(C=C) and p(C–C) for these molecules from their molecular orbitals, as is shown in Table 3. This calculation suggests that the extra electron causes a decrease in p(C=C) of 0.13 and an increase in p(C–C) of 0.12, compared to the values of p-chloranil. These results are in good agreement with those evaluated from the infrared spectra.

There is a well-known relation between the bond order and the bond length, l, of a carbon-carbon bond.[12)] This was illustrated in the upper part of Fig. 4. In this relation, p(C=C) and p(C–C) derived from the infrared spectra give l(C=C) and l(C–C) respectively. These values of l(C=C) and l(C–C) for p-chloranil and its anion-radical are collected in Table 4. The estimated l(C=C) and l(C–C) values of p-chloranil are in good agreement with the results of the X-ray study.[7)] Table 4 shows that the unpaired electron on the anion-radical may cause an increase of 0.01 Å in l(C=C) and a decrease of 0.02 Å in l(C–C), compared to the values of p-chloranil. However, no observation of the molecular structure of the anion-radical has yet been made.

Carbon-Oxygen Bond. If we take $K_s=5.0$ md/Å and $K_d=10.7$ for C=O bond, values proposed by Bratoz and Besnainou,[14)] and neglect the contribution of the self-polarizability to the stretching force constant, those force constants for p-chloranil and its anion-radical give the values of p(C=O) as 0.82 and 0.40 respectively. These values should be compared with those of 0.91 and 0.79 respectively calculated from their molecular orbitals. In p-chloranil, the agreement is rather satisfactory.

[14)] S. Bratoz and M. S. Besnainou, *J. Chem. Phys.*, **34**, 1142 (1961).

TABLE 4. THE VALUES OF THE BOND LENGTHS OF l(C=C) AND l(C–C) FOR *p*-CHLORANIL AND ITS ANION-RADICAL
(in unit of Å)

Bond	*p*-Chloranil		*p*-Chloranil$^-$	
	IR[a]	Obsd[b]	IR[a]	Obsd[c]
C–C	1.47	1.477	1.45	(1.44)
C=C	1.36	1.342	1.37	(1.38)

a) The values estimated from the bond orders, which were derived from the stretching force constants in the infrared spectra.

b) The observed values by the X-ray study; see Ref. 7.

c) The values estimated in the *p*-benzoquinone anion-radical from its molecular orbitals; see O. Kikuchi and K. Someno, This Bulletin, **40**, 2972 (1967).

Although there is a definite trend towards less bond order, no quantitative agreement is obtained for the anion-radical. One reason for this might be the neglect of the self-polarizability.

As for the relation between the force constant and the bond length of a C=O bond, Badger proposed the following equation:[15]

$$K(\mathrm{C{=}O}) = 1.86/\{l(\mathrm{C{=}O})-0.68\}^3, \qquad (3)$$

where K and l are in md/Å and Å units respectively. For *p*-chloranil and its anion-radical, the values of l(C=O) derived from their force constants by Eq. (3) were 1.26 Å and 1.31 Å respectively. The former value is rather larger than the observed value of 1.195 Å.[7] Although the agreement is not satisfactory, we may expect than the C=O bond length of the anion-radical is longer than that of *p*-chloranil by 0.05 Å; however, no experimental result is available at present.

Concluding Remarks. The present investigation clearly shows that the predominant factor in the frequency differences between *p*-chloranil and its anion-radical is the difference in their electronic structures. Nevertheless, we noticed some disagreements between the C=O bond orders obtained from their infrared spectra and those obtained from their molecular orbitals. We consider that these disagreements may be caused by the frequency shifts due to the crystal-field effect as well as by the neglect of the self-polarizability. The crystal-field effect may be more important for the ion-radical salts than for neutral molecular crystals.

Rigorously speaking, the $\boldsymbol{G}$ matrix for the anion-radical is not identical with that for *p*-chloranil, since the bond lengths of the anion-radical estimated from the bond orders were found to be slightly different from those of *p*-chloranil. The difference in their $\boldsymbol{G}$ matrices may make some contribution to the frequency difference. However, this contribution is negligibly small for the bands due to the stretching modes.

The set of force constants presented in Table 2 cannot be regarded as a unique solution. In this sense, it is important to note the couplings between the stretching force constants and the other force constants. However, our primary interest exists in studying the difference in the force constants between *p*-chloranil and its anion-radical. We consider that the set of force constants presented here is reliable enough for this purpose.

In conclusion, the application of the infrared spectra of a neutral molecule and its ion-radical can bring about valuable knowledge as to their molecular and electronic structures, such as bond lengths and bond orders. It is interesting to see that their frequency differences give some information concerning the nature of the half-filled orbital in the ion-radical molecular orbitals.

The author would like to express his appreciation to Professor Yoshio Matsunaga and Dr. Takao Iijima for their kind advice regarding this work.

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[15] R. M. Badger, *J. Chem. Phys.*, **3**, 710 (1935); see also J. A. Ladd, W. J. Orville-Thomas and B. C. Cox, *Spectrochim. Acta*, **20**, 1771 (1964).