BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2955—2959 (1973)

The Electronic States of *p*-Bromanil and Its Anion Radical as Studied by Means of Their Infrared Spectra

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(Received March 14, 1973)

The infrared spectra (400—4000 cm^{-1}) were measured with neutral *p*-bromanil and its anion radical. Appreciable frequency differences between their corresponding bands were observed. The fundamental frequencies were assigned, and the simple Urey-Bradley force fields were determined for both the neutral *p*-bromanil and its anion radical. The differences in the molecular and electronic structures between these two molecules were discussed on the basis of these results. The half-occupied molecular orbital of the *p*-bromanil anion radical was found to belong to the b_{3g} irreducible representation.

The infrared spectrum of an ion radical is known to be appreciably different from that of its neutral molecule.[1–12] The spectrum difference may be attributed to the difference in their intramolecular force fields. Up to now, however, attempts have scarcely been made to study such differences quantitatively.[8,12] In a previous paper,[8] we examined the infrared spectra (650—4000 cm^{-1}) of *p*-chloranil and its anion radical (see Fig. 1). In order to explain the appreciable frequency differences between their corresponding bands, the fundamental frequencies were assigned, and the simple Urey-Bradley force fields (UBFF's) were determined for both the neutral and anion radical molecules. It was found that the difference in the infrared spectra between these two molecules could be understood in terms of the difference in their electronic structures caused by the extra electron on the *p*-chloranil anion radical.[8,9]

In the present paper, the infrared spectra (400—4000 cm^{-1}) were measured with *p*-bromanil and its anion radical (see Fig. 1). In order to make vibrational assignments and to determine the force constants for these molecules, the normal coordinate treatments were carried out for the in-plane vibrations by using the simple UBFF's. The electronic states of the neutral *p*-bromanil and its anion radical were discussed on the basis of these experimental and theoretical investigations. We shall examine how the extra electron on the anion radical causes the difference in the molecular and electronic structures between the neutral *p*-bromanil and its anion radical. On the other hand, the substituent effects upon the molecular and electronic structures of the halogen-substituted *p*-benzoquinones and their anion radicals are interesting in comparison with the results previously reported for *p*-chloranil and its anion radical.[8]

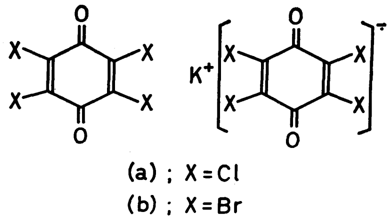

Fig. 1. (a) *p*-Chloranil and its anion radical salt with potassium cation, and (b) *p*-bromanil and its anion radical salt with potassium cation.

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Experimental

Materials. Commercially-available *p*-bromanil (Tokyo Kasei Kogyo Co., Ltd., GR grade) was used without further purification. Its anion radical salt with the potassium cation (K^+ *p*-Bromanil$^{\dot{-}}$) was synthesized according to the method of Torrey and Hunter.[13]

Measurements. The infrared spectra of these solid compounds were measured as Nujol mulls in the range from 400 to 4000 cm^{-1} using a Japan Spectroscopic Co., Ltd. IR-G infrared spectrometer. The infrared spectra in the regions where the absorption due to Nujol appears were measured using hexachlorobutadiene mulls. The spectra obtained for these compounds are reproduced in Fig. 2.

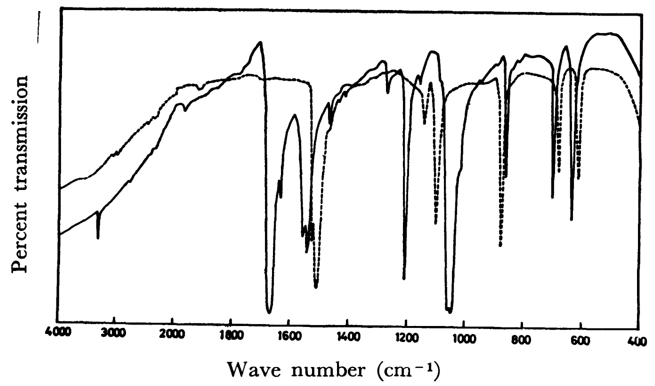

Fig. 2. The infrared spectra of *p*-bromanil and its anion radical salt with potassium cation.
———: *p*-Bromanil, ·········: K^+ *p*-Bromanil$^{\dot{-}}$

Since the counter cation of the salt is a simple alkali metal cation, the observed spectrum of K^+ *p*-Bromanil$^{\dot{-}}$ in the region under investigation should be due to that of the *p*-bromanil anion radical itself. The values of the absorption peaks observed for the neutral *p*-bromanil and its anion radical are listed in Table 1.

Table 1. The observed and calculated frequencies (cm^{-1}) for in-plane fundamental vibrations of the infrared spectra of the neutral *p*-bromanil and its anion radical[a)]

The neutral *p*-bromanil		Its anion radical		Assign.
Obsd	Calcd	Obsd	Calcd	
1672(s)	1672	1515(s)	1507	B_{2u}, $\nu(C=O)$
1565(s)	1557	1531(s)	1528	B_{3u}, $\nu(C=C)$
1549(s)				
1212(s)	1212	1150(w)	1256 (?)	B_{3u}, $\nu(C-C)$
1066(s)	1060	1105(s)	1098	B_{2u}, $\nu(C-C)$
1054(s)				
869(m)	869	879(s)	870	B_{2u}, $\left\{\begin{matrix}\nu(C-C)\\ \nu(C-Br)\end{matrix}\right.$
705(m)		684(m)		
650(m)	650	618(m)	618	B_{3u}, $\nu(C-Br)$

a) s: strong, m: medium, w: weak.

Normal Coordinate Treatment for In-plane Vibrations

In the infrared spectra of neutral *p*-bromanil and its anion radical, we observed appreciable frequency differences between their corresponding bands. For example, the C=O stretching mode of 1672 cm^{-1} in the neutral *p*-bromanil was found to be considerably red-shifted to 1515 cm^{-1} in the anion radical. Since only the intramolecular vibrations are expected to appear in the region from 400 to 4000 cm^{-1}, we attributed the spectrum difference between the neutral *p*-bromanil and its anion radical to the difference in their intramolecular force fields. The effect of crystal fields upon the vibrational frequencies is small in comparison with that of the intramolecular force fields. Therefore, to a first approximation, the contribution of the crystal fields to the spectra of *p*-bromanil and its anion radical was ignored in the present investigation.

The vibrational spectra of *p*-bromanil and its anion radical were then treated under the molecular point group, D_{2h}, and were analyzed by using a normal coordinate treatment. The molecular and crystal structures of the neutral *p*-bromanil have not yet been ascertained, although those of *p*-chloranil were determined by Chu, Jeffrey, and Sakurai.[14] It was assumed that the *p*-bromanil molecule was planar. By referring to the molecular structure of *p*-chloranil, the equilibrium bond lengths of *p*-bromanil were taken as $l(C=O)=1.195$ Å, $l(C=C)=1.342$, $l(C-C)=1.477$, and $l(C-Br)=1.89$, while the bond angles were taken as $\angle(O=C-C)=121°22'$, $\angle(C-C-Br)=116°15'$, and $\angle(C=C-Br)=122°23'$ (see Fig. 1). Since the structure of K^+ *p*-Bromanil$^{\dot{-}}$ has not yet been determined, it was assumed that the molecular structure of the anion radical was almost identical with that of the neutral *p*-bromanil. This assumption means that the ***G*** matrix calculated for *p*-bromanil was also used for its anion radical (see below). Hence, thirty normal modes of vibrations for *p*-bromanil or its anion radical were reduced to the symmetry species:

$$\begin{aligned}\Gamma &= 6A_g(R) + 5B_{1g}(R) + 5B_{2u}(IR) + 5B_{3u}(IR)\\ &\quad + 1B_{2g}(R) + 3B_{3g}(R) + 2A_u(\text{inactive}) + 3B_{1u}(IR),\end{aligned} \tag{1}$$

where the first four are the in-plane vibrations, and the rest, the out-of-plane vibrations. The signs of (R) and (IR) indicate the Raman and infrared active modes respectively. 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 ***GF*** matrix method was used in this work.[15] A representative example of each type of internal coordinate for the in-plane vibrations is given in Fig. 3. A simple UBFF was employed as the potential function. Then, four bond-stretching ($K(C=O)$, $K(C=C)$, $K(C-C)$ and $K(C-Br)$), five angle-bending ($H(O=C-C)$, $H(C-C-Br)$, $H(C=C-Br)$, $H(C-C-C)$ and H(C=

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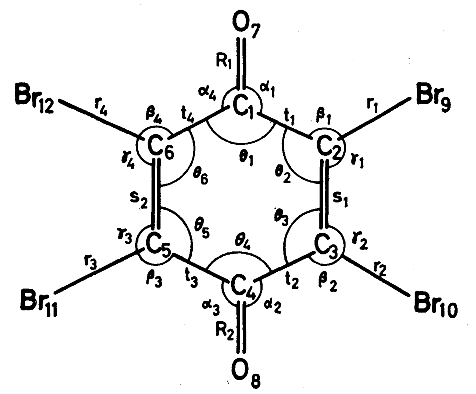

Fig. 3. The internal coordinates for the in-plane fundamental vibrations of *p*-bromanil or its anion radical.

C–C)), and five non-bonded repulsion force constants (*F*(O=C–C), *F*(C–C–Br), *F*(C=C–Br), *F*(C–C–C), *F*(C=C–C)) were necessary. At this time, it was assumed that the stretching force constants of *p*-bromanil were different from those of its anion radical, while the other force constants remained almost constant. Within the framework of this approximation, we could well explain the difference in the observed fundamental frequencies between *p*-bromanil and its anion radical. The trial force constants for *p*-bromanil were taken by referring to the values for benzene, halogen-substituted benzenes, *p*-benzoquinone, and *p*-chloranil,[8,16–18] while those for the *p*-bromanil anion radical were taken by modifying the force constants for the neutral *p*-bromanil. Refinements of the force constants were then carried out by the trial-and-error method, making use of the Jacobian matrix. The final sets of force constants thus obtained for the neutral *p*-bromanil and its anion radical are given in Table 2, while the frequencies calculated with these constants are compared in Table 1 with the observed values. In both of these molecules, the calculated values of the fundamental vibrations were found to agree well with the observed values, except for the following two points, which remain to be elucidated:

(1) Two absorption peaks were observed, at 705 cm^{-1} and 650 for the neutral *p*-bromanil or at 684 cm^{-1} and 618 for its anion radical, while only one fundamental vibration was expected to appear around this region.[19] It seems improbable to assign one of them to an out-of-plane vibration, because such a vibration would not appear around this region.

(2) The calculated 1256 cm^{-1} band in the anion radical cannot be assigned to any of the observed bands, presumably because of its weak intensity.

TABLE 2. THE FORCE CONSTANTS ESTIMATED FOR THE NEUTRAL *p*-BROMANIL AND ITS ANION RADICAL (md/Å)[a)]

Force constant	The neutral *p*-bromanil	Its anion radical
K(C=O)	9.62	7.10
K(C=C)	6.67	6.26
K(C–C)	2.96	3.33
K(C–Br)	2.63	2.17
H(O=C–C)	0.32	0.32
H(C–C–Br)	0.050	0.050
H(C=C–Br)	0.042	0.045
H(C–C–C)	0.210	0.237
H(C–C=C)	0.205	0.284
F(O=C–C)	0.801	0.793
F(C–C–Br)	0.710	0.710
F(C=C–Br)	0.710	0.710
F(C–C–C)	0.300	0.300
F(C–C=C)	0.370	0.500

a) $F' = -0.1\,F$.

Discussion

The Electronic States of p-*Bromanil and Its Anion Radical.* Since a total of 14 force constants of *p*-bromanil or its anion radical were evaluated from an experimental assignment of 6 frequencies, we suspect that these values of the force constants are not the best ones for these compounds. However, the stretching force constants are still meaningful, because the observed fundamental frequencies are almost all due to the bond-stretching modes. Therefore, below, we will discuss only the difference in the stretching force constants between the neutral *p*-bromanil and its anion radical. As is shown in Table 2, *K*(C=O)=9.62 md/Å, *K*(C=C)=6.67, *K*(C–C)=2.96, and *K*(C–Br)=2.63 for the neutral *p*-bromanil, while *K*(C=O)=7.10 md/Å, *K*(C=C)=6.26, *K*(C–C)=3.33, and *K*(C–Br)=2.17 for its anion radical. We can see that an extra electron on the *p*-bromanil anion radical markedly causes a decrease in the *K*(C=O), *K*(C=C) and *K*(C–Br) values and an increase in the *K*(C–C) value.

It is well known that the stretching force constant, $K(12)$, of a bond (12) in a conjugated system is greatly affected by its bond order, $p(12)$. According to Coulson and Longuet-Higgins,[20] $K(12)$ can be expressed by

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

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

In a homopolar carbon-carbon bond, the second

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

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

19) In *p*-chloranil, the corresponding bands were observed at 752 cm^{-1} and 715, and in its anion radical, at 725 cm^{-1} and 694. It appears that the bands at 752 cm^{-1} and 725 in *p*-chloranil and its anion radical shift to 650 cm^{-1} and 618 in *p*-bromanil and its anion radical, respectively, but it is not adequate to consider such band shifts in the cases of the other bands. Therefore, the bands at 650 cm^{-1} and 618 in *p*-bromanil and its anion radical were assigned to the fundamental vibrations of the C–Br stretching mode. See Ref. 8.

20) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. Ser. A,* **193**, 456 (1948).

term involving the self-polarizability may be small.[21] In this case, the stretching force constant, $K(12)$, is predominantly determined by the bond order, $p(12)$. By the use of the empirical relationship between $K(12)$ and $p(12)$ given in a previous paper,[8] we can evaluate the bond orders of the C=C and C–C bonds in *p*-bromanil and its anion radical. From the values of K(C=C) and K(C–C) in the infrared spectra, the p(C=C) and p(C–C) values for the neutral *p*-bromanil were estimated to be 0.88 and 0.27 respectively, while those for its anion radical were estimated to be 0.82 and 0.36 respectively. Therefore, we can see that the extra electron on the *p*-bromanil anion radical causes a decrease in p(C=C) by 0.06 and an increase in p(C–C) by 0.09. On the other hand, in order to confirm these results, we further calculated the p(C=C) and p(C–C) values of the neutral *p*-bromanil and its anion radical by the use of the molecular orbitals. For the sake of simplicity, the SCF molecular orbitals of the neutral *p*-benzoquinone calculated by Kunii and Kuroda (see Fig. 4) were used,[22] because the electronic state of the π-conjugated system in *p*-bromanil can be regarded as very similar to that in *p*-benzoquinone. It was also assumed that the extra electron of the anion radical enters into the lowest vacant molecular orbital of the neutral *p*-benzoquinone. As is shown in Fig. 4, this orbital has the irreducible representation of the symmetry, b_{3g}, where the coefficients of the C_1, C_2, and O_7 atomic orbitals were given by $+0.35887$, $+0.31428$, and -0.41674 respectively.[22] From the molecular orbital method, the p(C=C) and p(C–C) values for the neutral *p*-bromanil were estimated to be 0.91 and 0.30 respectively, while those for its anion radical were estimated to be 0.81 and 0.41 respectively. Therefore, the extra electron causes a decrease in p(C=C) by 0.10 and an increase in p(C–C) by 0.11 compared to the values of the neutral *p*-bromanil. These molecular orbital results are found to agree well with those evaluated from the infrared spectra.

Next, let us examine the heteropolar C=O bond. If we take, in Eq. (2), the values of $K_s = 5.0$ md/Å and $K_d = 10.7$ proposed by Bratoz and Besnainou,[23] and if we neglect the contribution of the self-polarizability to K(C=O), those C=O stretching force constants for *p*-bromanil and its anion radical give the values of p(C=O) of 0.81 and 0.37 respectively. These values should be compared with those of 0.85 and 0.70 respectively calculated from their molecular orbitals. In the neutral *p*-bromanil, the agreement is rather satisfactory. Although the extra electron definitely decreases the C=O bond order, no quantitative agreement is obtained in the anion radical. One reason for this might be the neglect of the self-polarizability.

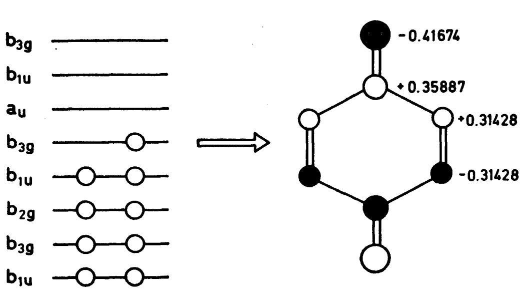

Fig. 4. Schematic representation of the molecular orbitals of the *p*-benzoquinone anion radical molecule. For the half-occupied molecular orbital with the b_{3g} irreducible representation, the open and closed circles indicate that the coefficients of the atomic orbitals are positive and negative, respectively. See text.

As for the C–Br bond, although the description of K(C–Br) *versus* p(C–Br) for the neutral *p*-bromanil and its anion radical is not simple, the extra electron on the *p*-bromanil anion radical causes a decrease in K(C–Br); this decrease will definitely lead to a decrease in p(C–Br). However, the estimation of p(C–Br) by the molecular-orbital method is rather complicated, because we have some difficulties in finding appropriate parameters for the Br atomic orbitals.

Some Information on the Molecular Structures of p-*Bromanil and Its Anion Radical.* There is a well-known relation between the bond order, $p(12)$, and the bond length, $l(12)$, of a carbon-carbon bond (12); this was first derived by Coulson.[21,24] By using this relationship, the p(C=C) and p(C–C) values estimated from the infrared spectra give l(C=C) and l(C–C) respectively. The l(C=C) and l(C–C) values for the neutral *p*-bromanil were thus estimated to be 1.35_6 Å and 1.47_5 respectively, while those for its anion radical were estimated to be 1.36_8 Å and 1.45_6 respectively. The values of the neutral *p*-bromanil are in good agreement with those of l(C=C) = 1.342 Å and l(C–C) = 1.477 respectively, which were employed in the previous calculation. We can further see that the extra 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*-bromanil. However, no observation of the molecular structure has yet been made for the anion radical.

As for the relation between the stretching force constant and the bond length of a C=O bond, Badger proposed the following equation:[25]

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

where K and l are in md/Å and Å units respectively. For *p*-bromanil and its anion radical, the values of l(C=O) derived from their force constants by Eq. (3) are 1.26 Å and 1.32 respectively. The former value is rather larger than the observed value of 1.195 Å. We may expect that the C=O bond length of the *p*-bromanil anion radical is longer than that of its neutral molecule by 0.06 Å; however, no experimental result is available at present.

Although we have no information on the relation between the stretching force constant and the bond length of the C–Br bond, the extra electron on the *p*-bromanil anion radical probably causes the difference in l(C–Br)

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

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[25] 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).

between *p*-bromanil and its anion radical.

Comparison with the Results of p-*Chloranil and Its Anion Radical.* In a previous paper,[8] the values of the stretching force constants for the neutral *p*-chloranil were reported to be K(C=O)=9.7 md/Å, K(C=C)=6.6, K(C–C)=3.0, and K(C–Cl)=2.67, while those for its anion radical were reported to be K(C=O)=7.3 md/Å, K(C=C)=6.1, K(C–C)=3.5, and K(C–Cl)=2.67. In comparison with those of the neutral *p*-bromanil and its anion radical, we can see that, in either the neutral molecule or its anion radical, the stretching force constants of the benzoquinone system are scarcely affected by replacing the chlorine substituents by the bromine substituents. This means that the molecular and electronic structures of the benzoquinone systems of *p*-bromanil and its anion radical are very similar to those of *p*-chloranil and its anion radical respectively. Although the previous paper described that the extra electron on the *p*-chloranil anion radical did not decrease the K(C–Cl) value,[8] this description is no longer adequate. More accurate assignments of the fundamental frequencies of *p*-chloranil and its anion radical will show the decrease in the K(C–Cl) value in the anion radical; this situation seems to be analogous to that of *p*-bromanil and its anion radical.

Concluding Remarks

The present investigation clearly shows that the predominant factor in the difference in the vibrational spectra between the neutral *p*-bromanil and its anion radical can be understood in terms of the differences in their electronic structures. By using these differences, the half-occupied molecular orbital of the *p*-bromanil anion radical was found to belong to the b_{3g} irreducible representation. However, we noticed some disagreements between the C=O bond orders obtained from the infrared spectra and those obtained from the molecular orbitals. We consider that these disagreements may be caused not only by the neglect of the self-polarizability, but also by the frequency shifts due to the crystal-field effect. Although the crystal-field effect may be more important for the anion radical salt than for the neutral molecular crystal, this contribution to the frequency shifts of *p*-bromanil and its anion radical may be small in comparison with the difference in their intramolecular force fields.

Rigorously speaking, the ***G*** matrix for the anion radical is no longer identical with that for the neutral *p*-bromanil, since the molecular structure of the anion radical was found to be slightly different from that of the neutral *p*-bromanil. Although the difference in their ***G*** matrices may make some contribution to the frequency differences, this contribution can be disregarded for the bands due to the bond-stretching modes.

The set of force constants presented in Table 2 cannot be regarded as a unique solution, since the observations of the fundamental frequencies are limited to the infrared spectra. In this sense, it is quite desirable to measure the Raman spectra of *p*-bromanil and its anion radical. We consider, however, that the set of force constants presented here is reliable enough for studying the difference in the stretching force constants between the neutral *p*-bromanil and its anion radical.

In conclusion, the application of the infrared spectra of a neutral molecule and its ion radical can provide valuable knowledge on their electronic structures as well as on their molecular structures. It is interesting to see that their frequency differences give some information concerning the nature of the half-occupied orbital in the ion-radical molecular orbitals.