NOTES

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Infrared Spectrum and Electronic State of *p*-Iodanil

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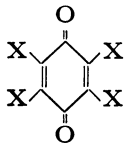
Synopsis. The infrared spectrum of *p*-iodanil was measured and the fundamental frequencies were assigned by using simple Urey-Bradley force field. The electronic state of *p*-iodanil was also discussed on the basis of those experimental results.

Halogen-substituted *p*-benzoquinones such as *p*-chloranil and *p*-bromanil (see Fig. 1) are known to be strong electron acceptor molecules, and much attention has been paid to the charge-transfer complexes with those acceptors.[1] However, only few attempts have been made to study the vibrational spectra of such acceptor molecules. In previous papers, we examined the infrared spectra of *p*-chloranil, *p*-bromanil, 2, 5-dibromo-3,6-dichloro-*p*-benzoquinone, and their anion radicals, and assigned their fundamental frequencies by using simple Urey-Bradley force fields (UBFF's).[2-4] This kind of investigation was found to be also very useful to study the electronic states of those π-conjugated *p*-benzoquinones, because the intramolecular force constants of those molecules are closely related to their electronic states. In the present paper, we examined the infrared spectrum and the electronic state of *p*-iodanil (see Fig. 1), which is one of the derivatives of iodo-substituted *p*-benzoquinones. It is interesting to compare the results of *p*-iodanil with those previously investigated for *p*-chloranil and *p*-bromanil.[2,3]



(a); X=Cl
(b); X=Br
(c); X=I

Fig. 1. Halogen-substituted *p*-benzoquinones; (a) *p*-chloranil, (b) *p*-bromanil, and (c) *p*-iodanil.

p-Iodanil was prepared by the reaction of *p*-bromanil with potassium iodide and sodium iodide and was crystallized from an ethyl acetate solution.[5] It was purified by sublimation *in vacuo*. The infrared spectrum of the solid *p*-iodanil was measured as Nujol mulls in the range from 400 to 4000 cm^{-1} using an IR-G infrared spectrophotometer (Japan Spectroscopic Co. Ltd.). The infrared spectrum in the regions where the absorption due to Nujol appears was measured using hexachlorobutadiene mulls. The observed absorptions are collected in Table 1.

Since only the intramolecular vibrations are expected to appear in the region from 400 to 4000 cm^{-1}, the vibrational spectrum of the solid compound can be approximately treated under the *p*-iodanil molecular point group D_{2h}. In order to understand the spectroscopic data, a normal coordinate treatment was made with *p*-iodanil molecule, and Wilson's ***GF*** matrix method was used for this purpose.[6] The structural data of *p*-iodanil were taken from those reported by Kobayashi *et al.*[7] Assuming that the *p*-iodanil molecule is planar, thirty normal modes of vibrations were reduced to the symmetry species:

$$\Gamma = 6A_g + 5B_{1g} + 5B_{2u} + 5B_{3u} + 1B_{2g} + 3B_{3g} + 2A_u + 3B_{1u}, \quad (1)$$

where the first four are the in-plane vibrations, and the rest, the out-of-plane vibrations. We calculated only the in-plane vibrations. A simple Urey-Bradley force field was employed as the potential function. The calculation process of the fundamentals of *p*-iodanil was very similar to the cases previously studied with *p*-chloranil and *p*-bromanil,[2,3] because the chloro-substituents or bromo-substituents were replaced by the iodo-substituents. Some of the force constants of *p*-iodanil could be transferred from those of *p*-chloranil or *p*-bromanil.[2,3] Refinements of the force constants were then carried out by the trial-and-error method making use of the Jacobian matrices. The calculated values of the *p*-iodanil fundamental vibrations with these force constants agreed well with the observed values. This is shown in Table 1 together with the assignments of the fundamental absorptions. In the following, we will only discuss the bond-stretching force constants, because the observed fundamentals arise mostly from the bond-stretching modes.

As for the C=O bond-stretching force constant, *K*-

Table 1. The observed and calculated frequencies (cm^{-1}) for the fundamental vibrations of *p*-iodanil

Obsd[a]	Calcd	Assignment
1659 (s)	1665	B_{2u}, ν(C=O)
1515 (s)	1506	B_{3u}, ν(C=C)
1192 (sh)		
1174 (s)	1167	B_{3u}, ν(C-C)
1161 (sh)		
1026 (sh), 1013 (s)	1024	B_{2u}, ν(C-C)
838 (w)		
833 (w)	838	B_{2u}, ν(C-C), ν(C-I)
824 (w)		
695 (s)		B_{1u}, out-of-plane
578 (sh), 567 (m)	562	B_{3u}, ν(C-I)

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

(C=O) of *p*-iodanil was estimated to be 9.56 mdyn/Å, whose value is close to the 9.7 value of *p*-chloranil or the 9.62 value of *p*-bromanil.[2,3] The C=C bond-stretching force constant, K(C=C), of *p*-iodanil was calculated to be 6.32 mdyn/Å, which is found to be somewhat smaller than the 6.6 value of *p*-chloranil or the 6.67 value of *p*-bromanil.[2,3] On the other hand, the C–C bond-stretching force constant, K(C–C), of *p*-iodanil was estimated to be 2.43 mdyn/Å. This value was found to be almost the same magnitude as those of the force constants for C–C single bonds of aliphatic hydrocarbons.[8] The C–C bond of *p*-iodanil appears to have more single bond character than have those of *p*-chloranil and *p*-bromanil. In fact, the C–C bond-stretching force constants of *p*-chloranil and *p*-bromanil have been estimated to be 3.0 mdyn/Å and 2.96, respectively[2,3]; these values are appreciably larger than the 2.43 mdyn/Å value for *p*-iodanil. In order to see this situation more quantitatively, the bond-stretching force constant, $K(12)$, in a π-conjugated system was related to the bond order, $p(12)$, and self-polarizability, $\pi(1212)$, of a bond (12) according to the Coulson and Longuet-Higgins formula:[9]

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

where s, d, K_s, and K_d are the bond lengths and the force constants associated with pure single and double bonds, respectively.

In a homopolar carbon-carbon bond, the second term involving the self-polarizability may be small.[2] By the use of the empirical relationship between $K(12)$ and $p(12)$ given in the previous paper,[2] we estimated the bond orders in *p*-iodanil as p(C=C)=0.82 and p(C–C) $\leq$0.15, respectively. Thus, the C–C bond of *p*-iodanil corresponds almost to pure single bond, and there is a strong alternation of the bond order between the C=C and C–C bonds. *p*-Iodanil appears to have more quinoid structure than has *p*-chloranil or *p*-bromanil.[2,3] This strong quinoid character of *p*-iodanil is also evidenced by the crystal structure analysis made by Kobayashi *et al.*[7] They reported the C–C bond length of *p*-iodanil to be 1.50 Å, which is as long as that of C–C pure single bond.

As for the heteropolar C=O bond, if we take, in Eq. 2, the values of K_s=5.0 mdyn/Å and K_d=10.7 proposed by Bratoz and Besnainou,[10] and if we neglect the contribution of the self-polarizability to K(C=O), the K (C=O) force constant of *p*-iodanil gives the value for the bond order of p(C=O)=0.80, which should be compared with p(C=O)=0.82 of *p*-chloranil or 0.81 of *p*-bromanil.[2,3]

The C–I bond-stretching force constant, K(C–I), of *p*-iodanil was estimated to be 1.43 mdyn/Å. This value was somewhat close to the value for the C–I bond-stretching force constant of alkyl iodides.[8]

We observed a strong absorption at 695 cm^{-1} in *p*-iodanil, but could not assign it to any of the in-plane fundamental vibrations. However, *p*-chloranil and *p*-bromanil have analogous absorptions at 715 cm^{-1} and 705, respectively,[2,3] and these absorptions show no appreciable frequency shifts in going from *p*-chloranil, *p*-bromanil to *p*-iodanil. Girlando *et al.* assigned the 715 cm^{-1} band of *p*-chloranil to the B_{1u} out-of-plane vibration of C=O bending mode.[11] Therefore, the same assignment is applicable to the 695 cm^{-1} absorption of *p*-iodanil.

In view of these results, the application of the infrared spectrum of *p*-iodanil is very useful to study the electronic states of the molecule. Kobayashi *et al.* have reported on some solid-state properties characteristic of *p*-iodanil.[7] In connection with the electronic states of the molecule, there remains a possibility that such properties may be induced by the strong quinoid structure of *p*-iodanil molecule.

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