The Electronic States of 2,5-Dibromo-3,6-dichloro-1,4-benzoquinone and Its Anion Radical as Studied by Means of Their Infrared Spectra

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The infrared spectra (400—4000 cm^{-1}) of neutral 2,5-dibromo-3,6-dichloro-1,4-benzoquinone and its anion radical were measured in order to observe the appreciable frequency differences between their corresponding bands. The vibrational assignments were made and the simple Urey-Bradley force fields were determined for both the neutral 2,5-dibromo-3,6-dichloro-1,4-benzoquinone and its anion radical. The differences in the molecular and electronic structures between these two molecules were investigated on the basis of these experimental and theoretical results. The half-occupied molecular orbital of the anion radical was found to belong to the b_g irreducible representation.

The infrared spectrum of an ion radical is known to be appreciably different from that of its neutral molecule.[1-13)] The spectrum difference seems to be attributable to the difference in their intramolecular force fields. Thus far, however, few attempts have been made to study such differences quantitatively.[8,12,13)] In previous papers,[8,13)] we examined the infrared spectra of *p*-chloranil (*p*-QCl_4), *p*-bromanil (*p*-QBr_4), and their anion radicals (see Fig. 1). For the neutral molecule and its anion radical, the fundamental frequencies were assigned and the simple Urey-Bradley force fields (UBFF's) were determined in order to explain the appreciable frequency differences between their corresponding bands.

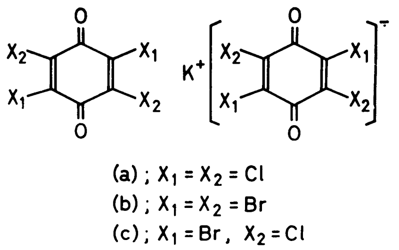

Fig. 1. The halogen-substituted *p*-benzoquinones and their anion radical salts with potassium cations; (a) *p*-chloranil, (b) *p*-bromanil and (c) 2,5-dibromo-3,6-dichloro-1,4-benzoquinone.

The present paper will describe the infrared spectra (400—4000 cm^{-1}) of neutral 2,5-dibromo-3,6-dichloro-1,4-benzoquinone (*p*-QBr_2Cl_2) and its anion radical (see Fig. 1). For these molecules, we also observed the appreciable frequency shifts between their corresponding bands. The normal coordinate treatments were carried out for the in-plane vibrations by using the simple UBFF's in order to make the vibrational assignments and in order to clarify the difference in the force constants between these molecules. It was shown that the force constants of *p*-QBr_2Cl_2 and its anion radical could be transferred from those of *p*-QX_4 ($X=Cl$ or Br) and its anion radical respectively, as estimated in previous papers.[8,13)] In this respect, it will be interesting to compare the effect of the symmetry degradation of *p*-QBr_2Cl_2 and its anion radical with that of the D_{2h} point group of *p*-QX_4 ($X=Cl$ or Br) and its anion radical. The electronic states of the neutral *p*-QBr_2Cl_2 and its anion radical will also be discussed on the basis of these experimental and theoretical investigations. We shall examine how the extra electron on the anion radical causes the differences in the molecular and electronic structures between the neutral *p*-QBr_2Cl_2 and its anion radical.

Experimental

Materials. The neutral *p*-QBr_2Cl_2 was synthesized by the bromination of 2,5-dichloro-1,4-benzoquinone. It was purified by recrystallization from benzene or glacial acetic acid. Its anion radical salt with the potassium cation (K^+ *p*-$QBr_2Cl_2^-$) was prepared according to the method of Torrey and Hunter.[14)]

Measurements. The infrared spectra of these solid compounds were measured as Nujol mulls in the range from 400 to 4000 cm^{-1} using a JASCO IR-G infrared spectrophotometer. Alternative measurements in the regions where the absorption due to Nujol appears were made using hexachlorobutadiene mulls. The spectra obtained for these compounds are reproduced in Fig. 2. Since the counter cation of the salt is a simple alkali metal cation, the observed spectrum of K^+ *p*-$QBr_2Cl_2^-$ in the 400—4000 cm^{-1} region is probably due to that of the *p*-QBr_2Cl_2 anion radical itself. The values of the absorption peaks observed for the neutral *p*-QBr_2Cl_2 and its anion radical are listed in Table 1.

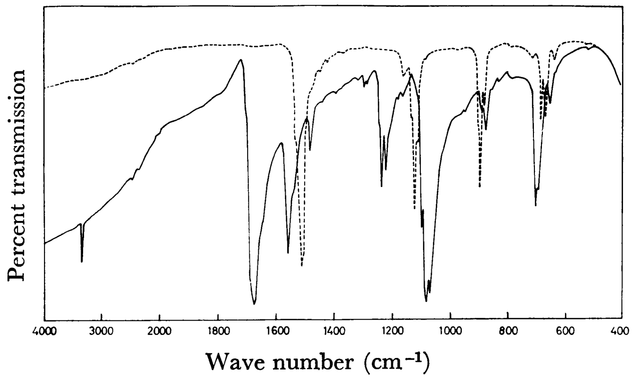

Fig. 2. The infrared spectra of 2,5-dibromo-3,6-dichloro-1,4-benzoquinone and its anion radical salt with potassium cation.
——: 2,5-dibromo-3,6-dichloro-1,4-benzoquinone
------: K^+ 2,5-dibromo-3,6-dichloro-1,4-benzoquinone$^-$

Table 1. The observed and calculated frequencies (cm^{-1}) for in-plane fundamental vibrations of the neutral p-QBr_2Cl_2 and its anion radical[a)]

Species		The neutral p-QBr_2Cl_2		Its anion radical	
		Obsd	Calcd	Obsd	Calcd
A_g	ν_1		1698		1433
	ν_2		1551		1604
	ν_3		1294		1348
	ν_4		930		930
	ν_5		840		831
	ν_6		740		741
	ν_7		471		476
	ν_8		311		313
	ν_9		281		281
	ν_{10}		201		203
	ν_{11}		125		126
B_u	ν_{12}	1675 (s)	1674	1514 (s)	1503
	ν_{13}	1560 (s)	1565	1535 (sh)	1537
	ν_{14}	1237 (s) 1223 (m)	1223	—	1263
		1099 (s)		1136 (sh)	
	ν_{15}	1083 (s)	1087	1124 (s)	1111
		1070 (s)		1115 (sh)	
	ν_{16}	890 (w) 877 (m)	892	898 (s) 884 (m)	886
	ν_{17}	708 (s) 697 (s)	696	689 (m) 672 (m)	671
	ν_{18}	—	400	—	397
	ν_{19}	—	338	—	335
	ν_{20}	—	182	—	183
	ν_{21}	—	121	—	122

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

Normal Coordinate Treatment for In-Plane Vibrations

In the infrared spectra of neutral p-QBr_2Cl_2 and its anion radical, we have observed appreciable frequency differences between their corresponding bands. For example, the C=O stretching mode of 1675 cm^{-1} in the neutral p-QBr_2Cl_2 is found to be considerably red-shifted to 1514 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 observed spectrum difference between the neutral p-QBr_2Cl_2 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-QBr_2Cl_2 and its anion radical was ignored in the present investigation.

The vibrational spectra of p-QBr_2Cl_2 and its anion radical were then treated under the molecular point group, C_{2h}, and were analyzed by using the normal coordinate treatment. The molecular and crystal structures of the neutral p-QBr_2Cl_2 have not yet been ascertained, although those of p-QCl_4 were determined by Chu, Jeffrey, and Sakurai.[15)] It was assumed that the p-QBr_2Cl_2 molecule was planar. By referring to the molecular structure of p-QCl_4, the equilibrium bond lengths of p-QBr_2Cl_2 were taken as $l(C=O)=1.195$ Å, $l(C=C)=1.342$, $l(C_1-C_2)=l(C_3-C_4)=1.477$, $l(C-Br)=1.89$, and $l(C-Cl)=1.714$, while the bond angles were taken as $\angle(O=C_1-C_2)=\angle(O=C_4-C_3)=121°22'$, $\angle(C-C-Br)=\angle(C-C-Cl)=116°15'$, and $\angle(C=C-Br)=\angle(C=C-Cl)=122°23'$ (see Fig. 1). Since the structure of K^+ p-$QBr_2Cl_2^{\cdot -}$ 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-QBr_2Cl_2. This assumption meant that the $\boldsymbol{G}$ matrix calculated for p-QBr_2Cl_2 was also used for its anion radical (see below).

By taking the molecular C_{2h} point group into consideration, thirty normal modes of fundamental vibrations for p-QBr_2Cl_2 or its anion radical are reduced to the symmetry species:

$$\Gamma = 11A_g(R) + 10B_u(IR) + 4B_g(R) + 5A_u(IR), \qquad (1)$$

where the first two 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. In connection with the number and species of the fundamentals for p-QX_4 (X=Cl or Br) and its anion radical, the correlation diagram between the C_{2h} and D_{2h} point groups is given in Table 2.

Table 2. The correlation diagram between the C_{2h} point group of p-QBr_2Cl_2 or its anion radical and the D_{2h} point group of p-QX_4, (X=Cl or Br), or its anion radical[a)]

C_{2h}	D_{2h}
A_g (11)	A_g (6)
	B_{1g} (5)
B_g (4)	B_{2g} (1)
	B_{3g} (3)
A_u (5)	A_u (2)
	B_{1u} (3)
B_u (10)	B_{2u} (5)
	B_{3u} (5)

a) The number in parentheses indicates that of the fundamental vibrations.

Wilson's $\boldsymbol{GF}$ matrix method was applied to p-QBr_2Cl_2 and its anion radical.[16)] We calculated only the in-plane vibrations, because no out-of-plane vibration is expected to appear in the region now under consideration. A simple UBFF was employed as the potential function. Note that the numbering of the carbon atoms in p-QBr_2Cl_2 or its anion radical is taken as 2,5-dibromo-3,6-dichloro-1,4-benzoquinone. Therefore, six bond-stretching ($K(C=O)$, $K(C=C)$, $K(C_1-C_2)$, $K(C_3-C_4)$, $K(C-Br)$, and $K(C-Cl)$), nine angle-bending ($H(O=C_1-C_2)$, $H(O=C_4-C_3)$, $H(C-C-Br)$, $H(C-C-Cl)$, $H(C=C-Br)$, $H(C=C-Cl)$, $H(C-C-C)$, $H(C_1-C_2=C_3)$, and $H(C_2=C_3-C_4)$) and nine non-bonded repulsion force constants ($F(O=C_1-C_2)$, $F(O=C_4-C_3)$, $F(C-C-Br)$, $F(C-C-Cl)$, $F(C=C-Br)$, $F(C=C-Cl)$, $F(C-C-C)$, $F(C_1-$

C_2=C_3), and $F(C_2{=}C_3{-}C_4)$) were necessary.

The trial force constants for the neutral p-QBr_2Cl_2 were transferred from the values for the neutral p-QX_4 (X=Cl or Br), while those for the p-QBr_2Cl_2 anion radical were transferred from the values for the p-QX_4 anion radical (X=Cl or Br).[8,13] For either the neutral p-QBr_2Cl_2 or its anion radical, it seems that $K(C_1{-}C_2) \approx K(C_3{-}C_4)$, $H(O{=}C_1{-}C_2) \approx H(O{=}C_4{-}C_3)$, $H(C_1{-}C_2{=}C_3) \approx H(C_2{=}C_3{-}C_4)$, $F(O{=}C_1{-}C_2) \approx F(O{=}C_4{-}C_3)$, and $F(C_1{-}C_2{=}C_3) \approx F(C_2{=}C_3{-}C_4)$. Refinements of the force constants were then carried out by the trial-and-error method, making use of the Jacobian matrix. In order to adjust the calculated frequencies to the observed fundamental frequencies, we paid much attention to the bond-stretching force constants, because the observed fundamental frequencies of the infrared spectra are almost all due to the bond-stretching modes. The final sets of force constants thus obtained for the neutral p-QBr_2Cl_2 and its anion radical are given in Table 3, while the frequencies calculated with these constants are in Table 1 compared with the observed values. In both of these molecules, the calculated vaues of the fundamental vibrations were found to agree well with the observed values, except for the following two points, which remain to be elucidated:

Table 3. Some of the force constants estimated for the neutral p-QBr_2Cl_2, p-QCl_4 and p-QBr_4 molecules and their anion radicals (md/Å)[a]

Force constant	Neutral molecule			Anion radical		
	p-QBr_2-Cl_2	p-QCl_4[b]	p-QBr_4[c]	p-QBr_2-Cl_2	p-QCl_4[b]	p-QBr_4[c]
$K(C{=}O)$	9.62	9.7	9.62	7.10	7.3	7.10
$K(C{=}C)$	6.67	6.6	6.67	6.26	6.1	6.26
$K(C_2{-}C_1)$	2.96	3.0	2.96	3.33	3.5	3.33
$K(C_3{-}C_4)$	2.96	3.0	2.96	3.33	3.5	3.33
$K(C{-}Br)$	2.63	—	2.63	2.17	—	2.17
$K(C{-}Cl)$	2.67	2.67	—	2.45	2.67	—

a) The values of the bending and non-bonded repulsion force constants for the neutral p-QBr_2Cl_2 were transferred from those for the neutral p-QCl_4 and p-QBr_4, while the values for the p-QBr_2Cl_2 anion radical, from those for the p-QCl_4 and p-QBr_4 anion radicals. See Refs. 8 and 13.

b) Ref. 8.

c) Ref. 13.

(1) In addition to the fundamental vibrations, shoulders or extra absorptions appear in both the neutral p-QBr_2Cl_2 and its anion radical. Some of them may arise from the splitting of the fundamental vibrations through the factor-group splitting.

(2) The calculated 1263 cm^{-1} band in the anion radical cannot be assigned to any of the observed bands, presumably because of its weak intensity.

Discussion

Comparison with the Results of p-QX_4 *(X=Cl or Br) and Its Anion Radical.* Since the observations of the fundamental frequencies are limited to the infrared spectra, we suspect that the sets of the force constants presented in Table 3 are not the best ones for either the neutral p-QBr_2Cl_2 or its anion radical. However, the stretching force constants are still meaningful, for 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-QBr_2Cl_2 and its anion radical. From Table 3, we can easily see that an extra electron on the p-QBr_2Cl_2 anion radical markedly causes a decrease in the $K(C{=}O)$, $K(C{=}C)$, $K(C{-}Br)$, and $K(C{-}Cl)$ values and an increase in the $K(C_1{-}C_2)$ and $K(C_3{-}C_4)$ values. Regardless of the symmetry degradation, this situation is very similar to that of the bond-stretching force constant difference between p-QX_4 (X=Cl or Br) and its anion radical reported in previous papers.[8,13] Table 3 clearly shows that the force constants of the neutral p-QBr_2Cl_2 are transferable from those of the neutral p-QCl_4 and p-QBr_4, and that the force constants of the anion radical of p-QBr_2Cl_2 are transferable from those of the p-QCl_4 and p-QBr_4 anion radicals. We can further see that, in spite of the symmetry degradation, the force constants of the benzoquinone system of the neutral p-QBr_2Cl_2 or its anion radical are scarcely affected by exchanging the chlorine substituents for the bromine substituents. This fact means that the carbon atoms bonded to the chlorine and bromine substituents are practically identical, and that the molecular structure and the force field for the benzoquinone system of the neutral p-QBr_2Cl_2 or its anion radical are very similar to those of the neutral p-QX_4 (X=Cl or Br) or its anion radical respectively.[8,13]

Although the previous paper stated that the extra electron on the p-QCl_4 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-QCl_4 and its anion radical show a decrease in the $K(C{-}Cl)$ value in the anion radical[17]; this situation seems to be analogous to that of p-QBr_2Cl_2 and its anion radical.

The Electronic States of p-QBr_2Cl_2 *and Its Anion Radical.* The electronic state of the neutral p-QBr_2Cl_2 differs from that of its anion radical, since the extra electron on the anion radical causes a marked decrease in the $K(C{=}O)$, $K(C{=}C)$, $K(C{-}Br)$, and $K(C{-}Cl)$ values and an increase in the $K(C_1{-}C_2)$ and $K(C_3{-}C_4)$ values. In this section, we shall investigate the electronic states of the neutral p-QBr_2Cl_2 and its anion radical by using the difference in their force constants.

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,[18] $K(12)$ 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), and s and d

are the bond lengths of pure single and double bonds respectively.

In a homopolar carbon-carbon bond, the second term involving the self-polarizability may be small.[19] In this case, the stretching force constant, $K(12)$, is predominantly determined by the bond order, $p(12)$. An empirical relationship between $K(12)$ and $p(12)$ has been given in a previous paper,[8] where several standard points of $K(12)$ and $p(12)$ were connected smoothly. This relationship enables us to evaluate the bond orders of the C=C, C_1–C_2, and C_3–C_4 bonds for p-QBr_2Cl_2 and its anion radical. From the values of $K(C=C)$, $K(C_1-C_2)$, and $K(C_3-C_4)$ in the infrared spectra, the $p(C=C)$, $p(C_1-C_2)$, and $p(C_3-C_4)$ values for the neutral p-QBr_2Cl_2 were thus estimated to be 0.88, 0.27, and 0.27 respectively, while those for its anion radical were estimated to be 0.82, 0.36, and 0.36 respectively. Therefore, the extra electron on the p-QBr_2Cl_2 anion radical was found to cause a decrease in $p(C=C)$ by 0.06 and an increase in $p(C_1-C_2)$ and $p(C_3-C_4)$ by 0.09.

On the other hand, let us examine the heteropolar C=O bond. If we take, in Eq. (2), the $K_s=5.0$ md/Å and $K_d=10.7$ md/Å values proposed by Bratoz and Besnainou,[20] and if we neglect the contribution of the self-polarizability to $K(C=O)$, those C=O stretching force constants for p-QBr_2Cl_2 and its anion radical give the values of $p(C=O)$ as 0.81 and 0.37 respectively. Therefore, the extra electron on the p-QBr_2Cl_2 anion radical definitely decreases the $p(C=O)$ values.

The values for the bond orders of the benzoquinone system of the neutral p-QBr_2Cl_2 and its anion radical were found to coincide well with those of the neutral p-QX_4 (X=Cl or Br) and its anion radical respectively.[21] We can further see that, for either of the neutral p-QBr_2Cl_2 or its anion radical, the $p(C_1-C_2)$ value is practically equal to the $p(C_3-C_4)$ value. For the molecular D_{2h} point group, the half-occupied molecular orbital in the p-QX_4 anion radical (X=Cl or Br) has been reported to belong to the b_{3g} irreducible representation.[8,13] The half-occupied molecular orbital of the p-QBr_2Cl_2 anion radical should belong to the b_g irreducible representation, since the point group of the anion radical is degraded into C_{2h}. This symmetry consideration of the half-occupied molecular orbital of the p-QBr_2Cl_2 anion radical is strongly supported by the fact that the extra electron on the anion radical causes a decrease in the $p(C=C)$ and $p(C=O)$ values and an increase in the $p(C_1-C_2)$ and $p(C_3-C_4)$ values compared to the values of the neutral p-QBr_2Cl_2. The electronic states of the benzoquinone system of the neutral p-QBr_2Cl_2 and its anion radical, although their point groups are degraded into C_{2h}, seem to be very similar to those of the neutral p-QX_4 (X=Cl or Br) and its anion radical respectively, which were reported in previous papers.[8,13]

As for the C–Cl and C–Br bonds, although the description of $K(C-X)$ *versus* $p(C-X)$ (X=Cl or Br) for the neutral p-QBr_2Cl_2 and its anion radical is not so simple, the extra electron on the p-QBr_2Cl_2 anion radical causes a decrease in $K(C-Cl)$ and $K(C-Br)$, which will definitely lead to a decrease in $p(C-Cl)$ and $p(C-Br)$. However, the estimation of $p(C-Cl)$ and $p(C-Br)$ by the molecular orbital method is rather complicated, for there are some difficulties in taking appropriate parameters for the Cl and Br atomic orbitals.

Some Information on the Molecular Structures of p-QBr_2Cl_2 *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); it was first derived by Coulson.[19,22] By using this relationship, the $p(C=C)$, $p(C_1-C_2)$, and $p(C_3-C_4)$ values estimated from the infrared spectra give $l(C=C)$, $l(C_1-C_2)$, and $l(C_3-C_4)$ respectively. The $l(C=C)$, $l(C_1-C_2)$, and $l(C_3-C_4)$ values for the neutral p-QBr_2Cl_2 were thus estimated to be 1.35_6, 1.47_5, and 1.47_5 Å, respectively, while those for its anion radical were estimated to be 1.36_8, 1.45_6, and 1.45_6 Å, respectively. The values of the neutral p-QBr_2Cl_2 are in good agreement with those of $l(C=C)=1.342$ Å, $l(C_1-C_2)=l(C_3-C_4)=1.477$ 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 $l(C_1-C_2)$ and $l(C_3-C_4)$ compared to the values of p-QBr_2Cl_2. 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:[23]

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

where K and l are in md/Å and Å units respectively. For p-QBr_2Cl_2 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-QBr_2Cl_2 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 lenght for the C–Cl and C–Br bonds, the extra electron on the p-QBr_2Cl_2 anion radical probably causes the difference in $l(C-Cl)$ and $l(C-Br)$ between p-QBr_2Cl_2 and its anion radical.

Concluding Remarks

In the present work, the difference in the vibrational spectra between the neutral p-QBr_2Cl_2 and its anion radical was interpreted in terms of the difference in their intramolecular force fields. On the other hand, the crystal-field effect may make some contribution to the frequency shifts in these vibrational spectra. Indeed, certain vibrational frequencies of the p-QBr_2Cl_2 anion radical salts will be influenced by the species of the counter cation. However, in a first approximation, this contribution can be neglected in comparison with that of the intramolecular force fields.

Rigorously speaking, the $\boldsymbol{G}$ matrix for the anion radical is not identical with that for the neutral p-QBr_2Cl_2, since the molecular structure of the anion radical will be slightly different from that of the neutral *p*-QBr_2Cl_2. The difference in their ***G*** matrices may make some contribution to the frequency difference. However, this contribution is negligibly small for the bands due to the bond-stretching modes.

The set of force constants presented in Table 3 cannot be regarded as a unique solution, since the observations for the fundamental frequencies are limited to the infrared spectra. In this sense, it is quite desirable to measure the Raman spectra of *p*-QBr_2Cl_2 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*-QBr_2Cl_2 and its anion radical.

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21) By using the relationship between $K(12)$ and $p(12)$, the values of the bond orders for the neutral *p*-QCl_4 have been reported to be $p(C=C)=0.87$, $p(C-C)=0.27$, and $p(C=O)=0.82$, while those for its anion radical, $p(C=C)=0.79$, $p(C-C)=0.37$ and $p(C=O)=0.40$. On the other hand, the values for the neutral *p*-QBr_4 were $p(C=C)=0.88$, $p(C-C)=0.27$ and $p(C=O)=0.81$, while those for its anion radical, $p(C=C)=0.82$, $p(C-C)=0.36$ and $p(C=O)=0.37$. See Refs. 8 and 13.

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