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The Electronic Spectra of the Anion Radical Salts Derived from 2,3-Dicyano-1,4-benzoquinone and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone[1]

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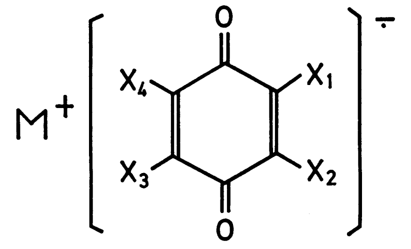
The anion radical salts derived from 2,3-dicyano-1,4-benzoquinone and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone were prepared. The absorption spectra in an acetonitrile solution and the solid-state spectra were examined for these anion radical salts. Unlike the absorption spectra in solution, in the solid-state spectra strong charge-transfer bands appeared and there were blue-shifts of the high-energy bands. These spectroscopic features were discussed on the basis of the charge-transfer interaction between the anion radicals. The solid-state properties of these salts were compared with those previously investigated for the anion radical salts of the halogen-substituted *p*-benzoquinones.

In general, solid ion radical salts have been a matter of great interest,[2–9] because the ion radical molecules form, in themselves, a plane-to-plane stacking into columns so as to make a large overlap between their half-filled molecular orbitals.[10] In this case, any individual ion radical molecule interacts through charge-transfer most strongly with one or two other radicals. In a previous paper,[7] the solid-state properties were examined for the anion radical salts of *p*-chloranil, 2,5-dibromo-3,6-dichloro-1,4-benzoquinone, and *p*-bromanil. The electronic spectrum of the solid salt was found to be different from the monomer spectrum of the anion radical in solution and to show the intermolecular charge-transfer band. The charge-transfer interaction between the anion radicals was much affected not only by the kinds of halogen substituents in the anion radical molecules, but also by the species of the counter cations.



(a) ; $X_1 = X_2 = X_3 = X_4 =$ Cl

(b) ; $X_1 = X_2 = X_3 = X_4 =$ Br

(c) ; $X_1 = X_3 =$ Br, $X_2 = X_4 =$ Cl

(d) ; $X_1 = X_2 =$ H , $X_3 = X_4 =$ CN

(e) ; $X_1 = X_2 =$ Cl , $X_3 = X_4 =$ CN

Fig. 1. The anion radical salts of (a) *p*-chloranil, (b) *p*-bromanil, (c) 2,5-dibromo-3,6-dichloro-1,4-benzoquinone, (d) 2,3-dicyano-1,4-benzoquinone, and (e) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. M^+ represents a diamagnetic counter cation.

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1) This work was presented at the Symposium on Molecular Structure, Sapporo, October, 1967.

2) W. J. Siemons, P. E. Bierstedt, and R. G. Kepler, *J. Chem. Phys.*, **39**, 3523 (1963).

3) R. G. Kepler, *ibid.*, **39**, 3528 (1963).

4) Y. Iida and Y. Matsunaga, This Bulletin, **41**, 2615 (1968).

5) Y. Iida, *ibid.*, **42**, 71 (1969).

6) Y. Iida, *ibid.*, **42**, 637 (1969).

7) Y. Iida, *ibid.*, **43**, 2772 (1970).

8) Y. Iida, *ibid.*, **44**, 663 (1971).

9) J. Tanaka and M. Mizuno, *ibid.*, **42**, 1841 (1969).

10) G. R. Anderson and C. J. Fritchie, Jr., Second National Meeting, Society for Applied Spectroscopy, San Diego, October, 14, Paper 111 (1963); C. J. Fritchie, Jr., *Acta Cryst.*, **20**, 892 (1966); C. J. Fritchie, Jr., and P. Arthur, Jr., *ibid.*, **21**, 139 (1966); P. Goldstein, K. Seff, and K. N. Trueblood, *ibid.*, **B24**, 778 (1968); J. Tanaka and N. Sakabe, *ibid.*, **B24**, 1345 (1968); H. Kobayashi, Y. Ohashi, F. Marumo, and Y. Saito, *ibid.*, **B26**, 459 (1970).

The present paper will describe some stable anion radical salts of cyano-substituted *p*-benzoquinones. The measurements of the solid-state spectra as well as the absorption spectra in an acetonitrile solution were attempted for the anion radical salts derived from 2,3-dicyano-1,4-benzoquinone (*p*-H_2QCy_2) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (*p*-Cl_2QCy_2). We shall examine how the charge-transfer interaction between the anion radicals contributes to the solid-state spectra of these anion radical salts. The solid-state spectra of these salts are interesting in comparison with those of the anion radical salts of the halogen-substituted *p*-benzoquinones.[7)]

Experimental

Materials. *p*-H_2QCy_2 was synthesized from *p*-benzoquinone according to the method of Thiele *et al.*,[11)] while *p*-Cl_2QCy_2 was commercially available. These compounds were purified by recrystallization from ethylene dichloride.

The following four anion radical salts were prepared according to the method of Matsunaga[12)]: Na^+ *p*-$Cl_2QCy_2^{-}$, K^+-*p*-$Cl_2QCy_2^{-}$, Na^+ *p*-$H_2QCy_2^{-}$ and K^+ *p*-$H_2QCy_2^{-}$. In this method, the anion radical salts were made by the one-electron reduction of the corresponding quinones with alkali metal iodides in an acetonitrile solution.

Measurements. The absorption spectra in an acetonitrile solution were measured at room temperature, using a Beckman DK-2A spectrophotometer at concentrations of the order of 10^{-4}—10^{-5} mol/*l*.

The diffuse reflection spectra of the solid salts were recorded on a Beckman DK-2A spectroreflectometer at room temperature in the range from 4.0 kK to 30.8 kK. In order to avoid cation exchange between the salt and the diluent, the sodium salts were ground and diluted with sodium chloride, while the potassium salts were similarly treated with potassium bromide. The solid-state spectra were then obtained by plotting the diffuse reflection spectra using the Kubelka-Munk equation, $f(R)=(1-R)^2/2R$, in which R is the reflectance. The experimental details were the same as those described in previous papers.[4-8)]

The Absorption Spectra in Solution

Some of the absorption spectra of these anion radical salts in an acetonitrile solution are reproduced in Fig. 2. The spectra are not changed when the counter cation of the salt is replaced. Since the concentrations are so dilute, the salts seem to be completely dissociated. The obtained spectra are those of the anion radical monomer, because the counter cations of the salts are simple alkali metal cations.

The p-Cl_2QCy_2 *Anion Radical (Fig. 2, Curve a).* This anion radical in an acetonitrile solution appears reddish violet, and is quite stable at room temperature. The absorption spectrum of the anion-radical monomer has absorption peaks at 17.1 kK and 18.3 kK, a band at 21.9 kK with a shoulder around 22.9 kK, and a strong absorption at 28.7 kK. These spectroscopic features are found to be in good accordance with those of the *p*-Cl_2QCy_2 anion radical previously reported by Iida and Akamatu,[13)] who produced the *p*-Cl_2QCy_2 anion radical by a one-electron transfer reaction from the 7,7,8,8-tetracyanoquinodimethane anion radical to *p*-Cl_2QCy_2 in an acetonitrile solution.

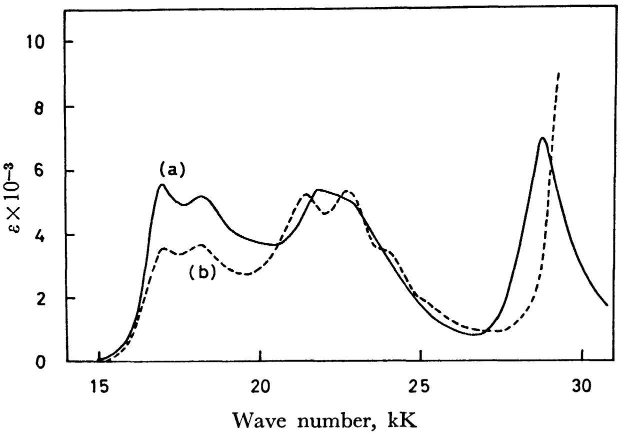

Fig. 2. The absorption spectra of (a) Na^{-} *p*-$Cl_2QCy_2^{-}$ and (b) Na^+ *p*-$H_2QCy_2^{-}$, in acetonitrile solution.

The p-H_2QCy_2 *Anion Radical (Fig. 2, Curve b).* This anion radical in an acetonitrile solution appears red, and is also quite stable at room temperature. The absorption spectrum of the anion radical monomer is composed of absorption peaks at 17.1 kK and 18.2 kK and at 21.5 kK and 22.7 kK, a shoulder around 23.9 kK, and a strong absorption in the energy region higher than 29 kK. Although this absorption spectrum seems to be similar to that of the *p*-Cl_2QCy_2 anion radical, the introduction of the chlorine substituents into the *p*-H_2QCy_2 anion radical causes some shifts in their corresponding bands. Unlike as in the *p*-Cl_2QCy_2 anion radical, the splitting of the band peaks at 21.5 kK and 22.7 kK and the shoulder around 23.9 kK are noted in the case of the *p*-H_2QCy_2 anion radical.

The Solid-State Spectra

Na^+ p-$Cl_2QCy_2^{-}$ *(Fig. 3, Curve a).* The solid-state spectrum of this salt shows a strong absorption at 12.6 kK and high-energy bands at 21.2 kK and 25.5 kK. This spectrum was found to be different from the monomer spectrum of the *p*-Cl_2QCy_2 anion radical in solution. The band at 12.6 kK appears in the low-energy region where the anion radical monomer does not absorb. This spectroscopic feature is very similar to that for the anion radical salts of halogen-substituted *p*-benzoquinones.[7)] The solid-state spectrum of Na^+ *p*-$Cl_2QCy_2^{-}$ can be compared with that of Na^+ *p*-Chloranil^{-}, since the *p*-Cl_2QCy_2 anion radical molecule is analogous to the *p*-chloranil anion radical. The value for the low-energy band at 12.6 kK of Na^+ *p*-$Cl_2QCy_2^{-}$ was found to be almost coincident with that for the band at 11.6 kK of Na^+ *p*-Chloranil^{-}, which is known, according to a previous investigation,[7)] to arise from the charge-transfer transition between the *p*-chloranil anion radicals in the solid state. The intensity of the

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[11)] J. Thiele and J. Meisenheimer, *Ber. Deut. Chem. Gesell.*, **33**, 675 (1900); J. Thiele and F. Günther, *Liebig's Ann. Chem.*, **349**, 59 (1906).

[12)] Y. Matsunaga, *J. Chem. Phys.*, **41**, 1609 (1964).

[13)] Y. Iida and H. Akamatu, This Bulletin, **40**, 231 (1967).

low-energy band for Na$^+$ p-Cl$_2$QCy$_2^-$ is as strong as that for Na$^+$ p-Chloranil$^-$. Judging from these results, the low-energy band at 12.6 kK for Na$^+$ p-Cl$_2$QCy$_2^-$ seems to be attributable to the charge-transfer transition between the p-Cl$_2$QCy$_2$ anion radicals. In this case, the p-Cl$_2$QCy$_2$ anion radicals will be stacked close enough together for the π orbitals to overlap, and the π–π transitions of the monomer will be perturbed in the field of the other anion radicals. This is shown as appreciable blue-shifts of the high-energy bands at 21.2 kK and 25.5 kK for the solid-state spectrum of Na$^+$-p-Cl$_2$QCy$_2^-$, compared to the monomer absorptions of the p-Cl$_2$QCy$_2$ anion radical at 17.1 kK and 21.9 kK respectively.

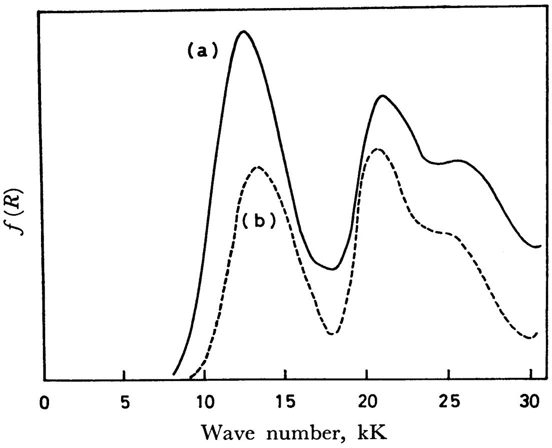

Fig. 3. The solid-state spectra of (a) Na$^+$ p-Cl$_2$QCy$_2^-$ and (b) K$^+$ p-Cl$_2$QCy$_2^-$.

K$^+$ p-Cl$_2$QCy$_2^-$ (Fig. 3, *Curve b).* The solid-state spectrum of this salt shows a low-energy band at 13.3 kK and high-energy bands at 20.7 kK and 25.0 kK. The locations of the band peaks for this salt were found almost to coincide with those for Na$^+$ p-Cl$_2$QCy$_2^-$. Although the intensity of the low-energy band for K$^+$ p-Cl$_2$QCy$_2^-$ is somewhat weaker than that for Na$^+$ p-Cl$_2$QCy$_2^-$, the electronic structures of the solid salts do not appreciably depend on the counter cations now under consideration.

Na$^+$ p-H$_2$QCy$_2^-$ (Fig. 4, *Curve a).* This salt gives the solid-state spectrum composed of a low-energy band at 10.7 kK with a shoulder around 14.3 kK, high-energy bands at 21.2 kK and 24.5 kK, and a shoulder in the energy region higher than 30.0 kK. Unlike as in Na$^+$ p-Cl$_2$QCy$_2^-$, not only the band peak at 10.7 kK but also the shoulder around 14.3 kK are noted for the charge-transfer bands of Na$^+$ p-H$_2$QCy$_2^-$. The intensities of these bands are quite strong. Although these bands are not completely resolved, they consist of two prominent peaks, and the splitting is approximately 3.6 kK. The energy of the first-band peak at 10.7 kK for Na$^+$ p-H$_2$QCy$_2^-$ is lower than that at 12.6 kK for Na$^+$ p-Cl$_2$QCy$_2^-$. Two charge-transfer absorptions are often observed for salts in which the charge-transfer interaction between the ion radicals is remarkably strong.[14] The charge-transfer interaction for Na$^+$ p-H$_2$QCy$_2^-$ appears to be stronger than that for Na$^+$ p-Cl$_2$QCy$_2^-$. The high-energy bands at 21.2 kK and 24.5 kK for the solid-state spectrum of Na$^+$ p-H$_2$QCy$_2^-$ can be assigned to the shifted bands of the p-H$_2$QCy$_2$ anion radical monomer at 17.1 kK and 21.5 kK respectively.

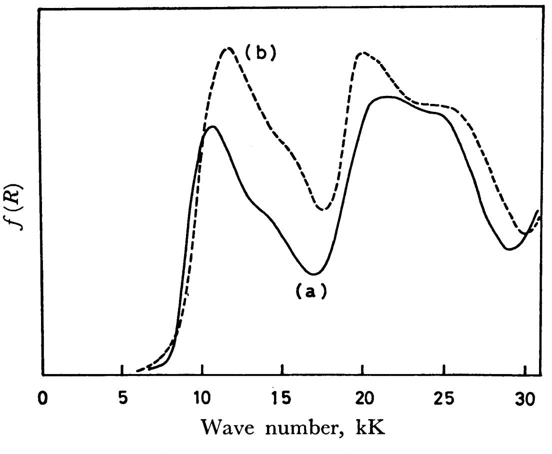

Fig. 4. The solid-state spectra of (a) Na$^+$ p-H$_2$QCy$_2^-$ and (b) K$^+$ p-H$_2$QCy$_2^-$.

K$^+$ p-H$_2$QCy$_2^-$ (Fig. 4, *Curve b).* This salt shows the solid-state spectrum composed of a low-energy absorption at 11.7 kK, a shoulder around 15.4 kK, high-energy bands at 20.0 kK and 25.0 kK, and a shoulder in the energy region higher than 30.0 kK. It is interesting to see that the spectroscopic features for this salt are similar to those for Na$^+$ p-H$_2$QCy$_2^-$. Therefore, the situations of the charge-transfer interaction for these substances seem to be much alike.

Discussion

The above-mentioned results of the solid-state spectra of these anion radical salts clearly show that a strong charge-transfer interaction takes place between the anion radical molecules. Therefore, the anion radical molecules can be expected to be stacked in a face-to-face manner and to form, in themselves, linear chain columns; this feature of the crystal structure has been found in a number of other ion radical salts.[10] The charge-transfer absorption characteristic of the solid salts should be ascribed to the transition of the type $<\cdots Q^-Q^-Q^-Q^-\cdots> \longrightarrow <\cdots Q^-Q^0Q^{2-}Q^-\cdots>$, where Q denotes a quinone molecule. However, a question still remains as to why the broad and doublet structure of the charge-transfer absorption appears in the p-H$_2$QCy$_2$ anion radical salts. A possible explanation has been proposed by Tanaka and Mizuno.[9] According to their discussion, if there are two sites in the one-dimensional radical column in a unit cell, there are two kinds of charge-transfer states; one is from the left site to the right site, and the other is from right to left. The splitting of the charge-transfer absorption occurs when one takes into consideration the interaction term between these two states. Although

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14) Two charge-transfer absorptions have also been observed for the solid-state spectra of the cation radical salts of p-phenylenediamine bromide and Würster's red bromide. In these solid salts, the charge-transfer bands are extraordinarily large, and the overlap integral between the half-filled molecular orbitals of the cation radicals is the largest in the series of Würster cation radical salts. See Refs. 4 and 9.

this off-diagonal element does not have terms proportional to the first order in the nearest neighbour electron overlap, it includes an electron-electron interaction of a dipolar type. With respect to the intermolecular separation between the anion radical molecules, the p-H_2QCy_2 anion radicals should be stacked more closely than the p-Cl_2QCy_2 anion radicals, since the latter include the bulky chlorine substituents. Therefore, the splitting of the charge-transfer absorption seems to be more important for the p-H_2QCy_2 anion radical salts than for the p-Cl_2QCy_2 anion radical salts. This is in agreement with the experimental results of the charge-transfer absorptions.

On the other hand, the charge-transfer interaction between the anion radical molecules in these anion radical salts was found to be almost independent of the species of the counter cations under consideration. This fact is in contrast to that for the anion radical salts of halogen-substituted p-benzoquinones, where the charge-transfer interaction is much reduced in the potassium salts in comparison with that in the sodium salts.7)

In conclusion, the charge-transfer interaction between anion radical molecules was found to take place not only in the anion radical salts of halogen-substituted p-benzoquinones but also in the anion radical salts of cyano-substituted p-benzoquinones. This kind of interaction is regarded as characteristic of ion radical salts in general.