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The Physical Properties of the Anion Radical Salts Derived from 3,5,3′,5′-Tetrachloro-4,4′-diphenoquinone and 3,5,3′,5′-Tetrabromo-4,4′-diphenoquinone[1]

Yôichi IIDA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

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The anion radical salts derived from 3,5,3′,5′-tetrachloro-4,4′-diphenoquinone and 3,5,3′,5′-tetrabromo-4,4′-diphenoquinone were prepared. The absorption spectra in solution and the solid-state spectra were examined in order to study the solid-state properties characteristic of the anion radical salts. The measurements of the static magnetic susceptibilities and the electrical resistivities were also useful for this purpose. These physical properties were found to be based on the charge-transfer interaction between the anion radical molecules. It was suggested that, in these solid anion radical salts, the anion radical molecules might be stacked by a unique face-to-face arrangement in groups of two or an infinite number of molecular systems.

The solid-state properties of the anion radical salts of various halogen-substituted *p*-benzoquinones have been reported in a previous paper.[2] The present paper will describe some anion radical salts of the halogen-substituted 4,4′-diphenoquinones with diamagnetic counter cations (see Fig. 1). The electron spin resonance (ESR) spectra of these crystalline salts have already been examined by Matsunaga.[3]

In general, solid ion radical salts have been a matter of great interest, 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.[4] In this case, any individual radi-

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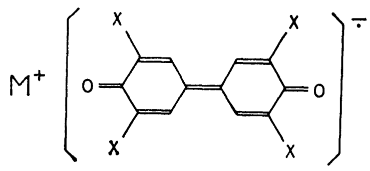
[1] This work was presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka (1968).

[2] Y. Iida, This Bulletin, **43**, 2772 (1970).

[3] Y. Matsunaga, *Canad. J. Chem.*, **38**, 1172 (1960).

[4] 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 Crystallogr.*, **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).



(a); X=Cl, (b); X=Br

Fig. 1. The anion radical salts of (a) 3,5,3′,5′-tetrachloro-4,4′-diphenoquinone (TCDQ) and (b) 3,5,3′,5′-tetrabromo-4,4′-diphenoquinone (TBDQ). M^+ represents a diamagnetic counter cation.

cal molecule interacts through charge transfer most strongly with one or two other radicals. Much knowledge concerning the mutual charge-transfer interaction has been accumulated by measuring the solid-state spectra, the magnetic susceptibilities, and the electrical conductivities.5–11) The purpose of the present paper is to apply these physical methods to the anion radical salts derived from 3,5,3′,5′-tetrachloro-4,4′-diphenoquinone (TCDQ) and 3,5,3′,5′-tetrabromo-4,4′-diphenoquinone (TBDQ). We shall examine how the charge-transfer interaction between the anion radicals contributes to the solid-state properties of these anion radical salts. The properties of these compounds are interesting in comparison with those previously-investigated properties of the halogen-substituted *p*-benzoquinone anion radical salts.2)

Materials

3,5,3′,5′-Tetrachlorobiphenyl-4,4′-diol was made by the chlorination of biphenyl-4,4′-diol (Eastman Kodak Co., white-label grade) suspended in acetic acid, while 3,5,3′,5′-tetrabromobiphenyl-4,4′-diol was similarly made by the bromination of biphenyl-4,4′-diol.12) The TCDQ and TBDQ13) were obtained by the oxidation of 3,5,3′,5′-tetrachlorobiphenyl-4,4′-diol and 3,5,3′,5′-tetrabromobiphenyl-4,4′-diol respectively with fuming nitric acid.12) They were purified by treating them with chloroform.

The following four anion radical salts were prepared according to the method of Matsunaga14): $\text{Na}^+\ \text{TCDQ}^{\bar{\cdot}}$, $\text{K}^+\ \text{TCDQ}^{\bar{\cdot}}$, $\text{Na}^+\ \text{TBDQ}^{\bar{\cdot}}$, and $\text{K}^+\ \text{TBDQ}^{\bar{\cdot}}$. In this method, the anion radical salts were made by the one-electron reduction of the corresponding quinones with alkali metal iodides in an acetone solution.

The Absorption Spectra in Solution

In order to characterize the solid-state spectra of these anion radical salts, it will be necessary to compare them with the absorption spectra of the salts dissolved in solution; therefore, we will examine the spectra in this section. The absorption spectra in solution were measured at room temperature, using a Beckman DK-2A spectrophotometer at concentration of the order of 10^{-5} mol/*l*. Since the anion radical salts are soluble only with difficulty in an acetone solution, it was difficult to determine the values for the molar extinction coefficients.

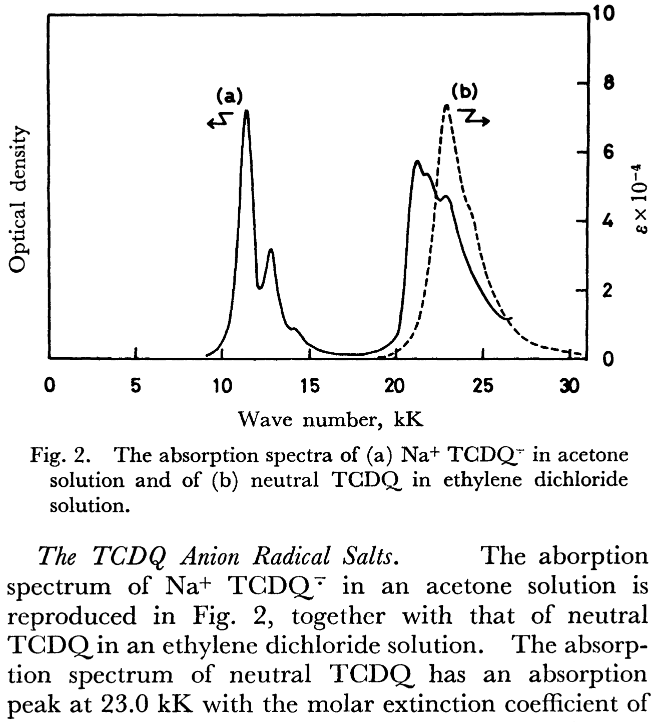


Fig. 2. The absorption spectra of (a) $\text{Na}^+\ \text{TCDQ}^{\bar{\cdot}}$ in acetone solution and of (b) neutral TCDQ in ethylene dichloride solution.

The TCDQ Anion Radical Salts. The aborption spectrum of $\text{Na}^+\ \text{TCDQ}^{\bar{\cdot}}$ in an acetone solution is reproduced in Fig. 2, together with that of neutral TCDQ in an ethylene dichloride solution. The absorption spectrum of neutral TCDQ has an absorption peak at 23.0 kK with the molar extinction coefficient of 7.33×10^4 and a shoulder around 24.2 kK, while that of the anion radical salt has low-energy absorption peaks at 11.4 kK, 12.9 kK, and 14.2 kK, and a high-energy band with some vibrational structures at 21.2 kK, 21.8 kK, and 22.9 kK. This anion radical salt in solution appears greenish yellow, and it is quite stable at room temperature. The spectrum is not changed when the counter cation of the salt is replaced by the potassium cation. Since the concentration is so dilute, the salt seems to be completely dissociated in the solution. The spectrum obtained is that of the anion radical

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

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

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

8) Y. Iida, *ibid.*, **42**, 71, 637 (1969).

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

10) Y. Iida, *ibid.*, **44**, 1777 (1971).

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

12) L. M. Jackman, "Advances in Organic Chemistry," Vol. II ed. by R. A. Raphael, E. C. Taylor, and H. Wynberg, Interscience Publishers, New York (1960) p. 329.

13) Generally speaking, stable anion radicals are made from strong electron-acceptor molecules. Both TCDQ and TBDQ molecules are strong electron acceptors. In order to investigate their electron-accepting properties, the charge-transfer complexes of TCDQ and TBDQ with such donors as aromatic hydrocarbons were examined in an ethylene dichloride solution. The absorption spectra of the complexes were measured at room temperature. The complex of pyrene with TCDQ showed the maximum position of the charge-transfer band at 14.2 kK, while the complex of pyrene with TBDQ showed it at 13.6 kK. Let us compare these results with the charge-transfer absorption of the pyrene-7,7,8,8-tetracyanoquinodimethane complex, where the absorption maximum of the first charge-transfer band has been reported to be located at 13.7 kK. For a common donor, the variation of the charge-transfer energies of the complexes arises mostly from the difference in the electron affinities of the acceptors. Therefore, if the value of 1.7 eV for the electron affinity of 7,7,8,8-tetracyanoquinodimethane is chosen as a reference, the electron affinities of TCDQ and TBDQ can be estimated to be 1.6_4 eV and 1.7_1 eV respectively. See Y. Iida, This Bulletin, **44**, 1430 (1971); G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).

14) Y. Matsunaga, *Nippon Kagaku Zasshi*, **89**, 905 (1968).

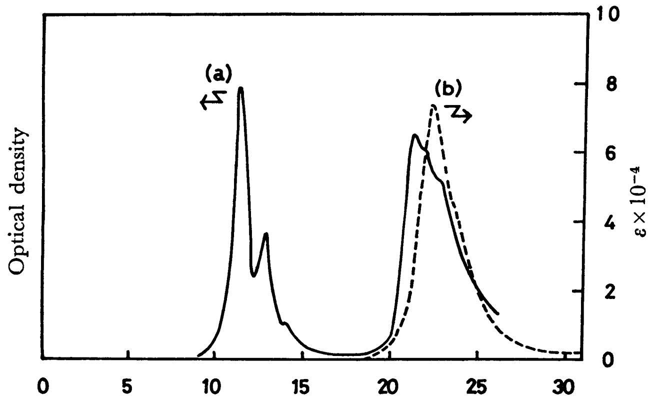

Fig. 3. The absorption spectra of (a) Na$^+$ TBDQ$^{\overline{\cdot}}$ in acetone solution and of (b) neutral TBDQ in ethylene dichloride solution.

monomer,[15] because the counter cations of the salts are simple alkali metal cations.

The TBDQ Anion Radical Salts. The absorption spectrum of Na$^+$ TBDQ$^{\overline{\cdot}}$ in an acetone solution is given in Fig. 3, together with that of neutral TBDQ in an ethylene dichloride solution. The absorption spectrum of neutral TBDQ has an absorption peak at 22.4 kK with the molar extinction coefficient of 7.40×10^4, and a shoulder around 23.5 kK, while that of the anion radical salt has low-energy absorption peaks at 11.4 kK, 12.9 kK, and 14.2 kK, and a high-energy band with some vibrational structures at 21.3 kK, 21.8 kK, and 22.9 kK.[15] The spectroscopic features of Na$^+$ TBDQ$^{\overline{\cdot}}$ were found to be very similar to those for Na$^+$ TCDQ$^{\overline{\cdot}}$. Therefore, it can be said that the electronic states of the 4,4′-diphenoquinone anion radicals are scarcely affected even though the chlorine substituents are replaced by the bromine substituents.

The Solid-State Spectra

In general, it is interesting to examine the solid-state spectra of ion radical salts if the charge-transfer interaction between the ion radicals takes place in the solid state. In this case, the solid-state spectra are known to be different from the monomer spectra of the ion radicals in solution and to show the intermolecular charge-transfer band in the low-energy region.[2,7–11] In this section, we will apply this method to the solid TCDQ and TBDQ anion radical salts by measuring the diffuse reflection spectra.

The diffuse reflection spectra were recorded on a Beckman DK-2A spectroreflectometer in the range from 4.0 kK to 30.8 kK at room temperature. 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 TCDQ Anion Radical Salts. These crystalline anion radical salts are dark blue and are quite stable at room temperature. The solid-state spectrum of Na$^+$ TCDQ$^{\overline{\cdot}}$ (Fig. 4, Curve a) shows a low-energy band at 6.6 kK and high-energy bands at 15.5 kK and 26.2 kK.[16] Theses pectroscopic features were found to be quite different from those of the monomer spectrum of the TCDQ anion radical in solution. The band at 6.6 kK appears in the low-energy region, where the anion radical monomer does not absorb. This band is broad without vibrational structures, and the intensity is strong. It cannot be assigned to the charge-transfer transition from the anion radical to the counter cation, since its maximum position is scarcely shifted when the counter cation of the salt is replaced (see below). Although, at present, no experimental data on the charge-transfer absorption in the dimer of the anion radicals are available for purposes of comparison, the low-energy band at 6.6 kK seems to be attributable to the charge-transfer transition between the anion radicals in the solid state. In this case, the TCDQ anion radicals will be stacked closely enough together for the half-filled molecular orbitals to make a large overlap, and the π-π transitions of the monomer will be much perturbed in the field of the other anion radicals. This is shown as appreciable blue-shifts of the high-energy bands at 15.5 kK and 26.2 kK for the solid-state spectrum of Na$^+$ TCDQ$^{\overline{\cdot}}$, compared to the monomer absorptions of the TCDQ anion radical at 11.4 kK and 21.2 kK respectively.

The solid-state spectrum of K$^+$ TCDQ$^{\overline{\cdot}}$ (Fig. 4, Curve b) shows a low-energy band at 6.7 kK and high-energy bands at 15.3 kK and 25.4 kK. The locations and the intensities of these bands were found to coincide well with those for Na$^+$ TCDQ$^{\overline{\cdot}}$. Therefore, the situation of the solid state of K$^+$ TCDQ$^{\overline{\cdot}}$ seems to be

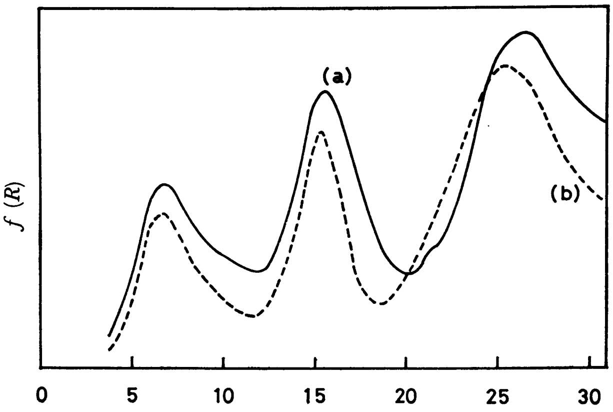

Fig. 4. The solid-state spectra of (a) Na$^+$ TCDQ$^{\overline{\cdot}}$ and (b) K$^+$ TCDQ$^{\overline{\cdot}}$.

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[15] The monomer spectrum of the 4,4′-diphenoquinone anion radical was found to be very similar to that of the benzidine cation radical. Concerning the π-electron systems, the 4,4′-diphenoquinone anion radical seems to be, in spite of the opposite electric charge, isoelectronic to the benzidine cation radical. See H. Matsusaka and K. Suzuki, paper presented at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966.

[16] The monomer spectrum and also the solid-state spectrum of the 4,4′-diphenoquinone anion radical salt were found to be very similar to those of the cation radical salt of benzidine bromide, respectively. The solid-state spectrum of the benzidine bromide shows a low-energy charge-transfer band at 6.7 kK and high-energy bands at 15.6 kK and 26.0 kK. See Refs. 7 and 15.

very analogous to that of Na$^+$ TCDQ$^{\overline{\cdot}}$.

The TBDQ Anion Radical Salts. These crystalline anion radical salts are also dark blue and are quite stable at room temperature. The solid-state spectrum of Na$^+$ TBDQ$^{\overline{\cdot}}$ (Fig. 5, Curve a) is composed of a low-energy band at 6.5 kK and high-energy bands at 15.1 kK and 25.5 kK.[16] These spectroscopic features were again found to be quite different from those of the monomer spectrum of the TBDQ anion radical in solution, but they were very similar to those of the solid-state spectrum of Na$^+$ TCDQ$^{\overline{\cdot}}$. Therefore, the low-energy band at 6.5 kK can also be assigned to the charge-transfer transition between the anion radicals in the solid state, while the high-energy bands at 15.1 kK and 25.5 kK can be assigned to the shifted bands of the monomer absorptions at 11.4 kK and 21.3 kK respectively. The electronic structures of the solid 4,4′-diphenoquinone anion radical salts are scarcely affected even though the chlorine substituents are replaced by the bromine substituents.

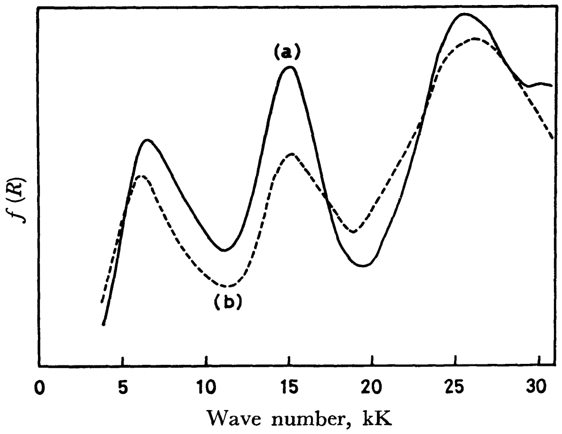

Fig. 5. The solid-state spectra of (a) Na$^+$ TBDQ$^{\overline{\cdot}}$ and (b) K$^+$ TBDQ$^{\overline{\cdot}}$.

K$^+$ TBDQ$^{\overline{\cdot}}$ gives a solid-state spectrum (Fig. 5, Curve b) comprising a low-energy charge-transfer band at 6.2 kK and high-energy bands at 15.2 kK and 25.8 kK. The locations and the intensities of these bands are coincident with those for the corresponding bands in Na$^+$ TBDQ$^{\overline{\cdot}}$. Therefore, the charge-transfer interactions in these two solid substances appear to be very much alike in manner.

The Magnetic Susceptibilities

It has been well established that the charge-transfer interaction between the ion radicals leads to a marked decrease in the paramagnetic susceptibilities of the ion-radical salts.[2,6–9] The charge-transfer interaction is known to stabilize the antiferromagnetic state where the spins associated with the ion radicals are antiparallel. Hence, we will attempt to measure the static magnetic susceptibilities for the TCDQ and TBDQ anion radical salts.

The magnetic susceptibilities of the anion radical salts and the neutral TCDQ and TBDQ were measured by the Gouy method. All the measurements were made at room temperature under an atmospheric pressure. The susceptibility balance was calibrated by referring to distilled oxygen-free water, for which the susceptibility was taken to be -0.720×10^{-6} emu/g at room temperature.

Na$^+$ TCDQ$^{\overline{\cdot}}$. Although the TCDQ anion radical molecule possesses an unpaired electron, the magnetic susceptibility of Na$^+$ TCDQ$^{\overline{\cdot}}$ at 18°C was found to be diamagnetic. Its value was experimentally determined to be $-(143\pm3)\times10^{-6}$ emu/mol, while the value for the neutral TCDQ was determined to be $-(142\pm1)\times10^{-6}$ emu/mol. The value for the neutral TCDQ was used for the diamagnetic susceptibility of its anion radical, since the skeleton of the neutral TCDQ is very similar to that of its anion radical. By making the correction for the diamagnetism of the counter cation, the diamagnetic susceptibility of Na$^+$ TCDQ$^{\overline{\cdot}}$ was estimated to be $-(147\pm1)\times10^{-6}$ emu/mol. The paramagnetic susceptibility of Na$^+$ TCDQ$^{\overline{\cdot}}$ was evaluated by subtracting the diamagnetic susceptibility from the observed magnetic susceptibility. The paramagnetic susceptibility was thus determined to be as small as $(4\pm4)\times10^{-6}$ emu/mol; this value corresponds only to $(0.3\pm0.3)\%$ of the free-spin paramagnetism. This marked disappearance of the paramagnetism can be understood in terms of the antiferromagnetic spin exchange interaction between the unpaired electrons on the TCDQ anion radicals. Although it is not clear, at present, whether the spin exchange interaction can be described by the singlet-triplet model or by the linear chain Heisenberg model, the antiferromagnetic spin exchange interaction in this salt seems to be as large as 0.1—0.2 eV. At any rate, it is certain that the charge-transfer interaction between the anion radicals makes a significant contribution to the antiferromagnetic spin exchange interaction.

Na$^+$ TBDQ$^{\overline{\cdot}}$. The magnetic susceptibility of Na$^+$ TBDQ$^{\overline{\cdot}}$ at 18 °C was also found to be diamagnetic. Its value was experimentally determined to be $-(155\pm2)\times10^{-6}$ emu/mol, while the value for neutral TBDQ was determined to be $-(174\pm1)\times10^{-6}$ emu/mol. In a way similar to the case of Na$^+$ TCDQ$^{\overline{\cdot}}$, the paramagnetic susceptibility of Na$^+$ TBDQ$^{\overline{\cdot}}$ was estimated to be $(24\pm3)\times10^{-6}$ emu/mol by subtracting the diamagnetic susceptibility of $-(179\pm1)\times10^{-6}$ emu/mol. The magnitude of this paramagnetic susceptibility, although it is rather larger than that of Na$^+$ TCDQ$^{\overline{\cdot}}$, is much less than that of the free-spin paramagnetism. Except for a slight decrease in the antiferromagnetic spin-exchange interaction in Na$^+$ TBDQ$^{\overline{\cdot}}$, the magnetic state of Na$^+$ TBDQ$^{\overline{\cdot}}$ appears to be similar to that of Na$^+$ TCDQ$^{\overline{\cdot}}$.

The Semiconductivities

Among the organic semiconductors, ion radical salts are known to exhibit particularly high electrical conductivities.[5] These electrical properties are based on a unique face-to-face stacking of the ion radical molecules in the solid state.[4] In this respect, it seemed that it would be interesting to examine the semiconductive properties of the TCDQ and TBDQ anion radical salts.

The electrical resistivity and its variation when the temperature ranged from 15 °C to 90°C were measured with the DC method. The anion radical salts have been available only as small crystals, excluding the possibility of single-crystal measurements. Hence, the measurements were performed with the sample powder under a compression of 5.4×10^2 kg per cm^2 between stainless steel electrodes in a Teflon cylinder.

For all of these compounds, a good linear relationship was obtained when the logarithm of the resistivity was plotted against the reciprocal of the absolute temperature. Therefore, the resistivity (ρ) was described by:

$$\rho = \rho_0 \exp{(E/kT)}, \qquad (1)$$

where E is the activation energy for conduction. For the TCDQ and TBDQ anion radical salts, the data on the specific resistivity at room temperature and the value of E are collected in Table 1. Table 1 shows that these values are scarcely affected when the substituents of the anion radicals or the counter cations now under investigation are replaced.

TABLE 1. THE ELECTRICAL RESISTIVITY DATA ON THE TCDQ AND TBDQ ANION RADICAL SALTS

Compound	ρ at 20°C (Ωcm)	E[a] (eV)
$\mathrm{Na^+TCDQ^{\overline{\cdot}}}$	2.0×10^4	0.24
$\mathrm{K^+TCDQ^{\overline{\cdot}}}$	3.3×10^4	0.24
$\mathrm{Na^+TBDQ^{\overline{\cdot}}}$	3.2×10^3	0.22
$\mathrm{K^+TBDQ^{\overline{\cdot}}}$	8.7×10^4	0.27

a) The activation energy for conduction.

These anion radical salts were found to be highly conductive. This implies the arrangement of a face-to-face stacking of the anion radical molecules in these solid salts. It is interesting to see that the specific resistivities of these anion radical salts are as low as those of the 7,7,8,8-tetracyanoquinodimethane (TCNQ) anion radical salts, in which the specific resistivities of $\mathrm{Na^+\,TCNQ^{\overline{\cdot}}}$ and $\mathrm{K^+\,TCNQ^{\overline{\cdot}}}$ have been reported to be 1×10^5 Ω cm and 1×10^4 Ω cm respectively at room temperature.[5]

Discussion

The above-mentioned characteristics in the solid-state spectra, the magnetic susceptibilities, and the electrical resistivities clearly indicate that the strong charge-transfer interaction between the anion radical molecules takes place in the TCDQ and TBDQ anion radical salts. Therefore, the anion radical molecules are expected to form, in themselves, a place-to-plane stacking into columns so as to make a large overlap between their half-filled molecular orbitals; this feature of the crystal structure has also been found in a number of other ion radical salts.[4] The charge-transfer absorption characteristic of the solid-state spectra should be ascribed to the transition of the $\langle\cdots Q^-Q^-Q^-Q^-\cdots\rangle \rightarrow \langle\cdots Q^-Q^0Q^{2-}Q^-\cdots\rangle$ type, where Q^- denotes a 4,4′-diphenoquinone anion radical molecule. However, a question still remains whether the intermolecular interaction is to be described predominantly by pair-by-pair or by a linear chain column composed of an infinite number of anion radical molecules. In the former case, the interaction is approximately confined to the dimer of the anion radicals, while, in the latter case, one individual anion radical interacts equally strongly with two others. In this respect, a further study of the X-ray diffraction will be required to determine by which arrangement the TCDQ and TBDQ anion radicals are stacked in the present solid salts.

Finally, we have to compare the results on the TCDQ and TBDQ anion radical salts with those previously determined for the anion radical salts of various halogen-substituted *p*-benzoquinones.[2] The charge-transfer interaction in the halogen-substituted *p*-benzoquinone anion radical salts is largely affected not only by the kinds of the halogen substituents in the anion radical molecules, but also by the species of the counter cations. In the case of the potassium cation, the interaction of the salt is markedly decreased compared to that of the sodium salt. Moreover, the charge-transfer interaction is decreased when the substituted chlorine for the anion radical molecule is replaced by bromine. In contrast to these halogen-substituted *p*-benzoquinone anion radical salts, it is noteworthy that the manner of the charge-transfer interaction in the TCDQ and TBDQ anion radical salts does not depend practically on the kinds of the halogen substituents in the anion radical molecules or on the species of the counter cations now under investigation.