Semiconducting Anion-radical Salts Derived from 3,3'5,5'-Tetrahalo-*p*-diphenoquinones[1)]

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3,3′,5,5′-Tetrachloro- and 3,3′,5,5′-tetrabromo-*p*-diphenoquinones were found to form series of complex anion-radical salts of the $M^+(Q_2)^-$ or $M^+_2(Q_3)^{2-}$ type with various onium cations. These complex salts are dark-colored, almost black in many cases, and show electronic absorptions extending into the rock-salt region. In addition, bluish green-colored simple salts could be isolated with a few cations. The complex salts exhibit electrical resistivities in orders from 10 to 10^4 ohm cm at room temperature. Neither the pattern due to the quinone molecule nor that due to the semiquinone ion is present in their vibrational spectra. A single carbonyl stretching vibration band appears around 1600 cm^{-1}, intermediate between that in the quinone and that in the semiquinone salt.

A new class of electrically-conducting organic compounds formed from various cations and the anion-radical of 7,7,8,8,-tetracyanoquinodimethane (TCNQ) was synthesized by Melby *et al.* about ten years ago.[2–4)] The composition of the anion-radical salts is represented by $M^+(TCNQ)_n^-$, where M^+ is a cation. Naturally, the value of *n* is 1 in many cases, but for some cations *n* was found to have multiple values such as 1 and 2, or 1 and 1.5. The complex salts with higher values of *n* tend to exhibit a lower electrical resistivity than the simple salt, $M^+(TCNQ)^-$.[5)] Since the work of Melby *et al*, the physical properties of the TCNQ anion-radical salts, especially the electrical, magnetic, and optical properties of the complex salts, have been quite extensively studied; however, only relatively few data have been published for new complex ion-radical salts,[6–14)] and far less even for those derived from compounds other than TCNQ.

Goan *et al.* have reported that *p*-chloranil forms molecular complexes with cobaltocene and nickelocene in a mole ratio of donor-to-acceptor of 1 : 2.[15)] The presence of these complexes has been subsequently confirmed by Brandon *et al.* and also by Watanabe *et al.*[16,17)] Their electrical resistivities have been found in the range from 10^4 to 10^6 ohm cm.[17,18)] On the basis of the vibrational spectra, these complexes may be better characterized as complex anion-radical salts containing onium cations. During the course of their work on pentalene derivatives, Le Goff and Lacount obtained a purple-black tetrabutylammonium anion-radical salt of the tetracyanodimethane derivative of dibenzopentalenoquinone. Its composition happened to be $M^+_2(Q_3)^{2-}$. Unfortunately, no resistivity has been reported for this complex salt.[19)] 9-Dicyanomethylene-2,4,7-trinitrofluorene (DTF) was prepared by Mukherjee and Levasseur some years ago. All the anion-radical salts with cations such as methyltriethylammonium, *N*-methyl-quinolinium, methyltriphenylphosphonium, and methyltriphenylarsonium ions have been reported to have the composition of $M^+(DTF)^-$.[20)] Dupuis and Néel have extended the work on the anion-radical salts of DTF and also prepared those of its tetranitro analog. Among the combinations with nineteen cations examined, the only complex (1 : 2) salt was obtained by the reaction between 1,2,3-trimethylbenzimidazolium iodide and DTF.[21)] Here again, the complex salt is much more conducting than the corresponding simple salt. They have observed 50 ohm cm for the 1 : 2 salt and 10^6 ohm cm for the 1 : 1 salt.[22)] A possible complex cation-radical salt has been found in the system of iodine-semiquinoid phenothiazine bromide. The minimum resistivity observed at the composition of $(\text{phenothiazine})_2^+(Br_2I)^-$ is about 4 ohm cm.[23)] Thus, apart from the above-mentioned TCNQ anion-radical salts, our

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[1)] A part of this work was carried out by Y. M. while employed at the Central Research Division of American Cyanamid Co., and was presented at Organic Crystal Symposium, Chicago, 1965.

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knowledge of complex ion-radical salts is very fragmentary and scanty. Therefore, it seemed that it would be very interesting to find out whether or not quinones, common electron acceptors which can be as strong as TCNQ and DTF if appropriately selected, can form series of complex anion-radical salts with various onium cations. As the alkali salts of 3,3′,5,5′-tetrahalo-*p*-diphenosemiquinones are known to be quite stable,[24,25] the parent quinones were our first choice.

Experimental

Materials. The examples of the anion-radical salts cover only a part of the compounds prepared in this work. However, they illustrate all of the various preparative procedures which we employed.

*Tetrahalo-*p*-diphenoquinones*: *p*-Biphenol was prepared by the decomposition of tetrazotized benzidine, as has been described by Hirsch, and then halogenated following the procedures reported by Magatti.[26,27] Oxidation to the quinones was carried out in glacial acetic acid by the addition of fuming nitric acid or in carbon tetrachloride with oxides of nitrogen.[28,29] Hereafter, tetrachloro- and tetrabromo-*p*-diphenoquinones will be abbreviated as TCDQ and TBDQ respectively.

Na^+TCDQ^-: Earlier this salt was prepared by the oxidation of tetrachloro-*p*-biphenol dissolved in an aqueous solution of sodium hydroxide with the ferricyanide ion.[25] In the present work, TCDQ was reduced by grinding with an excess of sodium iodide in the presence of acetone. The green crystalline powder was then thoroughly washed with acetone.

(Di-n-propylammonium)$_2$(TCDQ)$_3$: By treating a mixture of 100 mg of powdered TCDQ and 65 mg of di-*n*-propylammonium iodide with acetone, the reddish violet color of the quinone was changed quickly into the black of the anion-radical salt. The yield was 95%. The same product was obtained by the reaction of di-*n*-propylammonium iodide with a mixture of TCDQ and Na^+TCDQ^- suspended in acetonitrile. The complex salt is a purple-black crystalline powder. Found: C, 49.3; H, 4.0; Cl, 36.0%. Calcd for $2C_6H_{16}N \cdot 3C_{12}H_4Cl_4O_2$: C, 49.3, H, 3.8, Cl, 36.4%.

Tetraethylammonium (TCDQ)$_2$: A mixture of 98 mg of TCDQ and 76 mg of tetraethylammonium iodide was added to 20 m*l* of acetone, after which the solution was stirred for a half hour at room temperature. The purple-black solid was collected on a filter and dried in a vacuum desiccator. The yield was 55 mg. Found: C, 49.8; H, 3.6; Cl, 36.5%. Calcd for $C_8H_{20}N \cdot 2C_{12}H_4Cl_4O_2$: C, 49.6; H, 3.7; Cl, 36.6%.

Ferricinium (TCDQ)$_2$: Ferrocene (0.36 g (2 mmol)) was dissolved in 100 m*l* of acetone, and then pulverized TCDQ (1.28 g (4 mmol)) was added. After 5 minutes stirring, the black product was filtered and washed with acetone. The yield was 1.15 g. Found: C, 49.4; H, 2.1; Cl, 34.4%. Calcd for $C_{10}H_{10}Fe \cdot 2C_{12}H_4Cl_4O_2$: C, 49.2; H, 2.2; Cl, 34.4%. The following attempt to prepare the simple salt resulted in the formation of the above-mentioned complex salt. Ferricinium triiodide (2.27 g (4 mmol)) and Na^+TCDQ^- (1.04 g (3 mmol)) were mixed in 50 m*l* of acetonitrile. The suspension was stirred for one hour. Found, C 48.9, H 2.4, Cl, 33.6%. The quinone required for the formation of the complex salt was apparently supplied by the oxidation of the $TCDQ^-$ ion with air during the process of preparation.

Cobalticinium (TCDQ)$_2$: Cobalticinium triiodide, 1.71 g (3 mmol), TCDQ, 0.97 g (3 mmol), and Na^+TCDQ^-, 1.05 g (3 mmol) were mixed in 50 m*l* of acetonitrile. After the mixture had been stirred for a half hour, the black product was filtered and washed with acetone. The yield was 1.8 g. Found: C, 48.1; H, 2.1; Cl, 33.9%. Calcd for $C_{10}H_{10}Co \cdot 2C_{12}H_4Cl_4O_2$: C, 49.0; H, 2.2; Cl, 34.0%.

Tetra-n-propylammonium TBDQ: A portion of 150 mg (0.3 mmol) of powdered TBDQ was stirred for one hour with 120 mg tetra-*n*-propylammonium iodide in 20 m*l* of acetone. The bluish-green precipitate was washed with benzene, in which the salt is not soluble. The yield was 130 mg. Found: C, 42.0; H, 4.8; Br, 45.9%. Calcd for $C_{12}H_{28}N \cdot C_{12}H_4Br_4O_2$: C, 42.0; H, 4.7; Br, 46.6%. The corresponding TCDQ salt could be prepared by employing benzene instead of acetone as the reaction medium, but it was found to be too unstable to be examined further.

N-Methyl-acridinium TBDQ: Powdered TBDQ (150 mg (0.3 mmol)) was stirred for 40 min at room temperature with *N*-methyl-acridinium iodide (135 mg (0.5 mmol)) in 30 m*l* of acetone. The green crystalline powder was then filtered. Found: C, 44.7; H, 2.5; Br, 45.9%. Calcd for $C_{14}H_{12}N \cdot C_{12}H_4Br_4O_2$: C, 45.0; H, 2.3; Br, 46.0%.

(N-*Methyl-acridinium*)$_2$*(TBDQ)*$_3$: A portion of 100 mg (0.2 mmol) of pulverized TBDQ and one of 50 mg (0.15 mmol) of *N*-methyl-acridinium iodide were ground together and then stirred with 30 m*l* of acetonitrile for a half hour. The violet crystalline solid was filtered and washed with the solvent. The yield was 60 mg. Found: C, 41.0; H, 2.2; Br, 48.9%. Calcd for $2C_{14}H_{12}N \cdot 3C_{12}H_4Br_4O_2$: C, 40.7, H, 1.9; Br, 50.8%.

p-*Phenylenediamine (TBDQ)*$_2$: *p*-Phenylenediamine and TBDQ in a mole ratio of 1 : 2 were added to benzene. After stirring for 15 min, the black product was filtered and washed with benzene. Found: C, 33.0; H, 1.8; N, 3.2; Br, 57.0%. Calcd for $C_6H_8N_2 \cdot 2C_{12}H_4Br_4O_2$: C, 32.5; H, 1.5; N, 2.5; Br, 57.7%.

*Cobalticinium (*p*-chloranil)$_2$*: Cobalticinium triiodide (1.14 g (2 mmol)), *p*-chloranil (0.49 g (2 mmol)), and K^+-(*p*-chloranil)$^-$ (0.57 g (2 mmol)) were mixed in 50 m*l* of acetone and then stirred for a half hour. The brownish-yellow crystalline product was filtered and washed with acetone. Found: C, 38.9; H, 1.9; Cl, 41.4%. Calcd for $C_{10}H_{10}Co \cdot 2C_6Cl_4O_2$: C, 38.8; H, 1.5; Cl, 41.8%.

Measurements. The electrical resistivities, ρ, at room temperature were examined by a voltage-current method employing a cell similar to that designed by LaFlamme.[30] In some cases, a gradual increase in the resistivity was observed on standing; therefore, the measurements were carried out immediately after drying in a vacuum. The temperature-dependence was measured by a potential-probe method only for some highly-conducting salts. The activation energy for semiconduction, E, was calculated from $\rho = \rho_0 \exp(E/kT)$.

The electronic spectra of the solid salts were recorded by means of a Beckman DK-2A spectrophotometer with the aid of a reflectance attachment, and the vibrational spectra, as Nujol mineral oil mulls by means of a Jasco IR-G infrared spectrophotometer. The procedure in the former measurements was described in detail in our previous paper.[23]

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Results and Discussion

Syntheses. The interaction between pyrene and TCDQ (TBDQ) dissolved in chloroform generates a charge-transfer absorption, the maximum of which is located at 13.8 (13.6) kK. This value can well be compared with that of 13.7 kK given by the pyrene complex of tetracyanoethylene (TCNE) and that of 13.1 kK given by the complex of TCNQ dissolved in the same solvent. In other words, the present quinones are electron-acceptors as strong as those famous π-acids. Therefore, it is quite understandable that the quinone molecule oxidizes the iodide ion to free iodine and takes up the electron to form the semiquinone ion.

The major synthetic routes to the present anion-radical salts may be classified into the following three.

Method 1: As has been mentioned above, the iodide serves as the electron source for the formation of the semiquinone ion. This is the most general route for the preparation of both simple and complex salts.

Method 2: The complex salt is prepared by the metathesis of the triiodide and NaTCDQ (NaTBDQ) in the presence of TCDQ (TBDQ). If the quinone is omitted, the amount required for the formation of the complex salt is provided by the oxidation of the semiquinone ion with air in the process of stirring.

Method 3: When the cation source is given as a strong electron-donor, the salt may be prepared by oxidation-reduction, as exemplified by the synthesis of the ferricinium $(\mathrm{TCDQ})_2$. Despite the excess of the electron-donor, the reduction of TCDQ is limited to that which can be stabilized in the form of the complex salt.

With most of the onium cations, M^+, the quinones form only complex anion-radical salts represented by the formulas $\mathrm{M(TCDQ)_2}$ or $\mathrm{M_2(TCDQ)_3}$ and $\mathrm{M(TBDQ)_2}$ or $\mathrm{M_2(TBDQ)_3}$. All the complex salts are dark-colored-brown, violet, or black depending upon the kind of cation. When heated, most of the TCDQ salts show color-changes due to decomposition in the temperature-range of 150 to 180°C, while the TBDQ salts show changes in the range from 130 to 170°C. The treatment of TCDQ with tetra-*n*-propylammonium iodide gave a bluish-green product which was too unstable to be analysed. This is the only possible simple TCDQ salt observed in our experiment except those with alkali metal cations. Simple TBDQ salts could be isolated with five cations, namely, tetra-*n*-propylammonium, *N*-methyl-acridinium, *N*-methyl-lepidinium, *N*-methyl-, and *N*-ethyl-isoquinolinium cations. They are green or bluish green, as is the sodium salt. Among the above-mentioned cations, *N*-methyl-acridinium also gives a complex anion-radical salt. So far this is the only combination to be found which forms both simple and complex salts.

Electrical Resistivities. As is summarized in Tables 1 and 2, resistivity values in the range of 10^2—10^3 ohm cm are typical of most of the simple and complex salts examined here. The highest resistivity is exhibited by the simple TBDQ salt of tetra-*n*-propylammonium; however, no appreciable difference is observed in the pair of the simple and complex TBDQ salts of *N*-methyl-acridinium. The TBDQ salts tend to be slightly more conductive than the TCDQ salts. Thus, the TCDQ salts exhibiting resistivities about 100 ohm cm or less include only the following three; the complex salts of cobalticinium, ferricinium, and *p*-phenylenediamine cations. On the other hand, the corresponding complex TBDQ salts and four others, which contain n-$\mathrm{Pr_2EtNH}$, n-$\mathrm{Pr_3NH}$, $\mathrm{Me_3PhN}$, and $\mathrm{Et_3PhN}$ cations, are as conducting as the TCDQ salts mentioned above.

Table 1. Anion-radical salts derived from tetrachloro-*p*-diphenoquinone (TCDQ)

Cation	Composition	Resistivity (ohm cm)	Low-energy Band (kK)
Sodium	1 : 1	2×10^3	9.3
Triethylammonium	2 : 3	7×10^3	5.3
Tetraethylammonium	1 : 2	4×10^3	<4
Di-*n*-propylammonium	2 : 3	6×10^2 [a]	4.3
Methyldi-*n*-propylammonium	2 : 3	1×10^3 [b]	<4
Ethyldi-*n*-propylammonium	1 : 2	1×10^3 [c]	4.4
Tri-*n*-propylammonium	1 : 2	3×10^2 [d]	4.3
Tetra-*n*-propylammonium	1 : 1 (?)	too unstable to be examined	
Trimethylphenylammonium	2 : 3	6×10^2 [e]	4.4
Triethylphenylammonium	1 : 2	4×10^3	<4
p-Phenylenediamine	1 : 2	120	<4
Quinolinium	2 : 3	2×10^5	6.4
N-(*n*-Propyl)-quinolinium	2 : 3	1×10^3	4.3
N-Methyl-isoquinolinium	2 : 3	7×10^3	5.0
N-Ethyl-isoquinolinium	2 : 3	6×10^3	5.0
N-(*n*-Propyl)-isoquinolinium	2 : 3	3×10^3	4.8
Lepidinium	2 : 3	1×10^4	6.2
N-Methyl-lepidinium	2 : 3	1×10^4	4.6
N-Ethyl-lepidinium	2 : 3	7×10^4	5.0
N-Methyl-acridinium	2 : 3	3×10^3	4.7
N-Ethyl-acridinium	2 : 3	5×10^4	6.5
Ferricinium	1 : 2	24 [f]	<4
Cobalticinium	1 : 2	50 [g]	<4

a) Activation energy 0.21 eV, b) 0.37 eV, c) 0.17 eV, d) 0.18 eV, e) 0.19 eV, f) 0.08 eV, g) 0.07 eV.

In the study of the tetra-*n*-alkylammonium TCNQ salts, Kusakawa and Akashi have shown that the cation size influences the electrical resistivity as much as by a factor of 10^6.[13] Although the space effects observed in the present work are not large, we can point out some trends. The following orders may be noted in the series of the TCDQ complex salts: quinolinium> *N*-*n*-propylquinolinium, *N*-methyl-isoquinolinium> *N*-ethyl-isoquinolium> *N*-*n*-propyl-isoquinolinium, and *N*-methyl-acridinium< *N*-ethyl-acridinium. When ammonium ions are employed, the effects are more pronounced in the series of the TBDQ salts. The resistivity decreases in this order of the cations: $\mathrm{Pr_2NH_2}>\mathrm{Pr_2MeNH}>\mathrm{Pr_2EtNH}>\mathrm{Pr_3NH}$. Similarly, $\mathrm{Et_3NH}>\mathrm{Et_4N}$ and $\mathrm{Me_3PhN}>\mathrm{Et_3PhN}$. The last order is reversed in the TCDQ salts.

Table 2. Anion-radical salts derived from tetrabromo-*p*-diphenoquinone (TBDQ)

Cation	Composition	Resistivity (ohm cm)	Low-energy Band (kK)
Sodium	1 : 1	2×10^3	6.3
Triethylammonium	2 : 3	5×10^3	4.7
Tetraethylammonium	1 : 2	6×10^2	<4
Di-*n*-propylammonium	2 : 3	2×10^3	<4
Methyldi-*n*-propylammonium	2 : 3	1×10^3	<4
Ethyldi-*n*-propylammonium	1 : 2	140	4.3
Tri-*n*-propylammonium	1 : 2	120	4.4
Tetra-*n*-propylammonium	1 : 1	2×10^7	10.5
Trimethylphenylammonium	2 : 3	130	<4
Triethylphenylammonium	2 : 3	84	<4
p-Phenylenediamine	1 : 2	66	<4
N-(*n*-Propyl)-quinolinium	2 : 3	2×10^3	<4
N-Methyl-isoquinolinium	1 : 1	9×10^2	5.8
N-Ethyl-isoquinolinium	1 : 1	2×10^3	4.3
N-(*n*-Propyl)-isoquinolinium	2 : 3	2×10^3	<4
N-Methyl-lepidinium	1 : 1	2×10^3	5.8
N-Ethyl-lepidinium	2 : 3	6×10^4	4.8
N-Methyl-acridinium	1 : 1	3×10^3	5.6
	2 : 3	2×10^3	4.2
N-Ethyl-acridinium	2 : 3	4×10^3	<4
Ferricinium	1 : 2	32[a]	<4
Cobalticinium	1 : 2	103[b]	<4

a) Activation energy 0.07 eV, b) 0.10 eV.

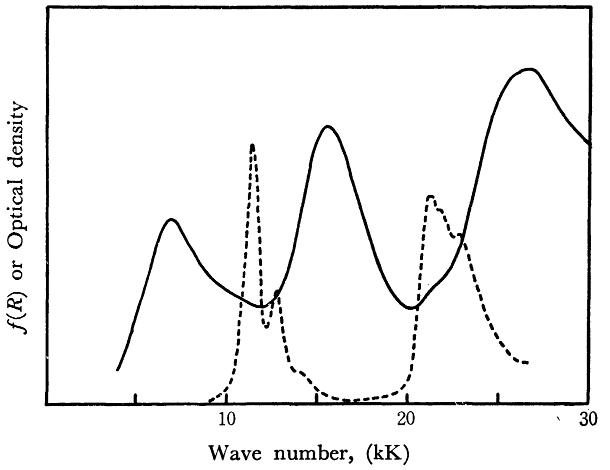

Fig. 1. Electronic spectra of Na^+TCDQ^- in the solid state (——) and in an acetone solution (----).

Electronic Spectra. As is shown in Fig. 1, the solid-state spectrum of NaTCDQ bears no resemblance to that of the salt dissolved in acetone. The solution spectrum comprises bands at 11.3 and 12.7, a shoulder at 14.0, and a strong band with some vibrational structures around 21 kK. It must be noted that this spectrum is very similar to that of the benzidine cation-radical cited in Fig. 2. The latter has bands at 11.6 and 13.1, a shoulder at 14.3, and a strong band around 21.6 kK.[31] Figure 2 presents

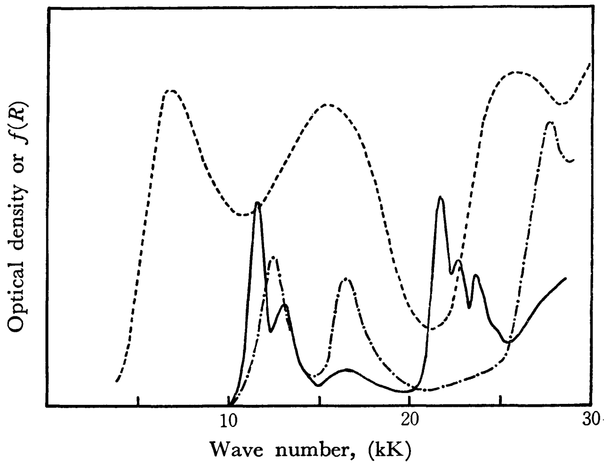

Fig. 2. Electronic spectra of benzidine bromide in an ethanolic solution at room temperature (——) and at low temperature (—•—•—) taken from Ref. 31, and the solid-state spectrum (----) taken from Ref. 32.

the solid-state spectrum of the benzidine bromide, which is very different from the spectra of not only the monomeric but also the dimeric forms of the cation-radical. Considering also the magnetic property, we concluded earlier that the univalent diamine cations in solid benzidine bromide is in a strong, more-than-by-pairs interaction.[32] The solid NaTCDQ shows a solid-state spectrum consisting of three bands located at 6.8, 15.5, and 26.4 kK. Again, this spectrum is very much like that of the benzidine bromide in the solid state. The latter spectrum, shown in Fig. 2, has three bands, at 6.7, 15.5, and 25.8 kK. Therefore, it seems to be quite certain that the anion-radicals in the solid NaTCDQ are also in a strong, more-than-by-pairs interaction. In accordance with this view, a relatively low resistivity, 10^3 ohm cm, is observed for this simple salt.

The spectrum of the solid NaTBDQ presented in Fig. 3 is composed three bands, at 6.2, 15.6, and about 27 kK, and is close to that of the solid NaTCDQ mentioned above. On the other hand, the simple bluish-

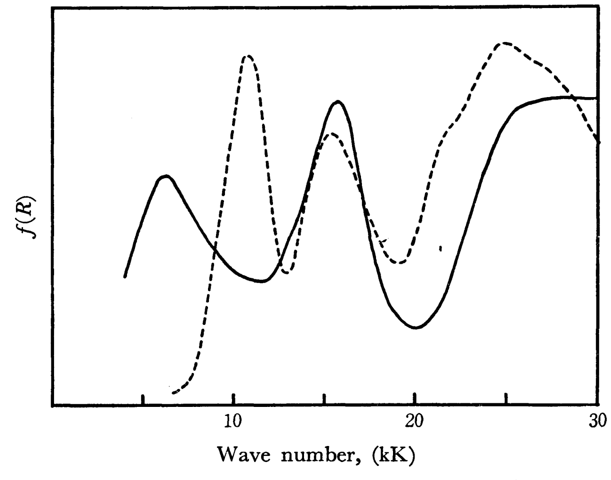

Fig. 3. Diffuse reflection spectra of Na^+TBDQ^- (——) and tetra-*n*-propylammonium-TBDQ (----).

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[32] Y. Iida and Y. Matsunaga, *ibid.*, **41**, 2615 (1968).

green TBDQ salt of tetra-*n*-propylammonium exhibits a resistivity as high as 10^7 ohm cm and a solid-state spectrum bearing no resemblance to that of the NaTBDQ. The bands in the spectrum of this ammonium salt are located at 11.5, 15.2, and 24.5 kK. This spectrum seems to correspond well to those of the dimeric form of the benzidine cation-radical: 12.4, 16.4, and 28 kK, as measured in a cold ethanolic solution (see Fig. 2), and 11.5, 15.2, and about 27 kK, as measured with colored acid clays moistened with benzene.[31,33] Thus, the anion-radicals here appear to be essentially in a pair-by-pair interaction. This speculation is consistent with the observed high resistivity.

The spectra of the simple and complex *N*-methyl-acridinium TBDQ salts are presented in Fig. 4. The simple salt exhibits a resistivity of 10^3 ohm cm, which can be well compared with that of NaTBDQ. However, their electronic spectra are different from each other. The *N*-methyl-acridinium salt shows a low-energy band at 5.6 kK, a little lower than that of the corresponding band of the sodium salt. In addition, the presence of an extra band at 10.5 kK must be noted. It is very likely that the interaction of the anion-radicals in this salt is also more-than-by-pairs, but in a mode somewhat different from that in NaTBDQ. The complex *N*-methyl-acridinium salt shows a spectrum consisting of four bands in the infrared and visible regions. The low-energy band appears at 4.2 kK, the limit of our spectrophotometer. The other three are located at 11.0, 18.2, and 24—28 kK. It is rather surprising to see that this spectrum is very much like that of the complex TCNQ salt of *N*-methyl-acridinium. The latter salt, with a composition of 1 : 2, exhibits four bands, located at <4, 11.2, 17.8, and 27.5 kK.[34] The spectra of most of the complex TCDQ (TBDQ) salts are more or less similar to the one shown in Fig. 4.

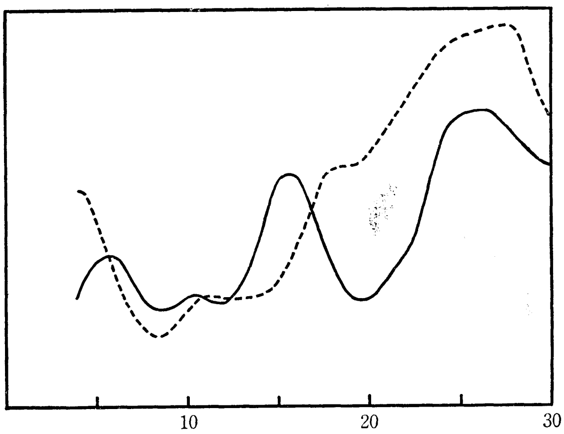

Fig. 4. Diffuse reflection spectra of *N*-methyl-acridinium-TBDQ, the simple salt (——) and the complex salt (----).

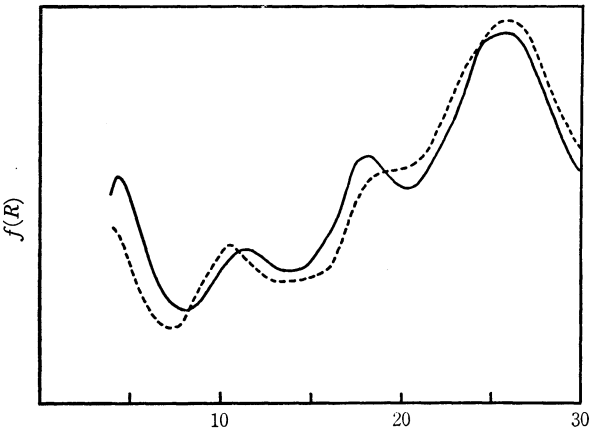

Fig. 5. Diffuse reflection spectra of the complex TCDQ salts containing ethyldi-*n*-propylammonium ion (——) and cobalticinium ion (----).

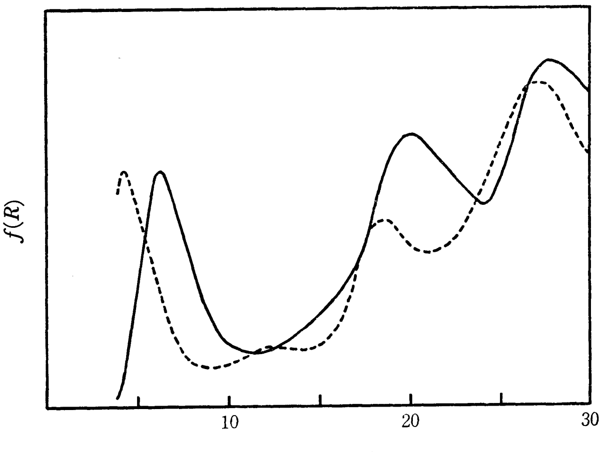

Fig. 6. Diffuse reflection spectra of the complex TCDQ salts containing quinolinium ion (——) and *N*-(*n*-propyl)-quinolinium ion (----).

Four more examples of the spectra of the complex TCDQ salts are presented in Figs. 5 and 6. In the cases shown in Fig. 5, the cations are quite different in nature and the compositions of the salts are not the same; however, all the patterns are very similar to one another. Absorption bands appear at 4.4, 11.4, 17.8, and 25.6 kK in the ethyldi-*n*-propylammonium salt and at <4, 10.5, 19.0, and 25.8 kK in the cobalticinium salt. On the other hand, the spectra of the TCDQ salts containing cations of the same nature, but exhibiting resistivities different by a factor of two hundred, are compared in Fig. 6. The less-conducting dark-brown-colored quinolinium salt shows bands at 6.4, 20.0 and 27.6 kK. Here, it seems that the weak second band is located around 15 kK, but is hidden by the strong third one. By the introduction of the *N*-*n*-propyl group, the bands are shifted to the low-energy side; that is, they appear at 4.3, 12.8, 18.5, and 27.4 kK. As a result, the salt is violet. In each combination of the salts shown in Figs. 5 and 6, it may be pointed out that the lower the resistivity, the less the energy of the first absorption band. However, such a tendency is only roughly observed in the other cases (see Tables 1 and 2).

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33) A. Hakusui, Y. Matsunaga, and K. Umehara, This Bulletin., **43**, 709 (1970).

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

For comparison with the complex anion-radical salts derived from TCDQ and TBDQ, the electronic spectra of the solid cobaltocene (p-chloranil)$_2$ and nickelocene (p-chloranil)$_2$ are shown in Fig. 7. The close agreement between these two suggests that the pattern is essentially determined by the interaction between p-chloranil and its anion-radical. Because of the presence of a wide, relatively transparent region, these salts are only lightly colored. However, it must be added that the presence of such a region is not characteristic of the complex salts. The simple sodium salt of p-chloranil, where the anion-radicals are supposed to be in a strong interaction, is known to exhibit absorption bands at 11.6 and 26.5 kK.[35] Compared with this, all the spectra of the complex salts are shifted to the low-energy side; the maxima of the strong bands in the cobalticinium salt are found at 5.6 and 22.2 kK.

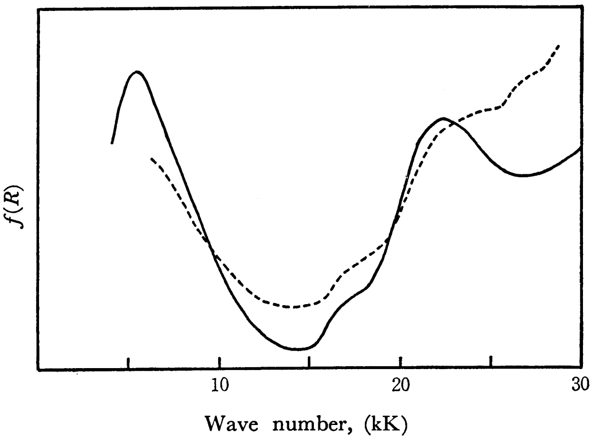

Fig. 7. Diffuse reflection spectra of cobaltocene (p-chloranil)$_2$ (——) and nickelocene (p-chloranil)$_2$ (----).

Vibrational spectra. It has been established that the vibrational spectrum of the semiquinone ion is markedly different from that of the parent quinone.[34,36] In Fig. 8, the spectrum of TCDQ is compared with that of its simple sodium salt. Instead of the normal carbonyl stretching vibration of TCDQ at 1640 cm^{-1}, a strong absorption band is observed 1530 cm^{-1} in the semiquinone salt. As the wavenumber of the carbonyl mode is known to be mainly determined by the bond order,[37–40] the observed shift can be attributed to the acceptance of one extra electron into the antibonding level of the TCDQ molecule. As a result, the carbonyl bonds more or less lose their double-bond character and the rings lose their quinoid structure. This change over the whole molecule leads to the drastic difference in the vibrational spectrum between the quinone and the semiquinone ion. Besides a large shift of the carbonyl stretching band, the appearance of a strong broad band at 1240 cm^{-1} must be considered as an indication of the reduction. Moreover, the shift of the band from 910 to 880 cm^{-1} and the replacement of a triplet around 800 cm^{-1} by a strong singlet must be noted.

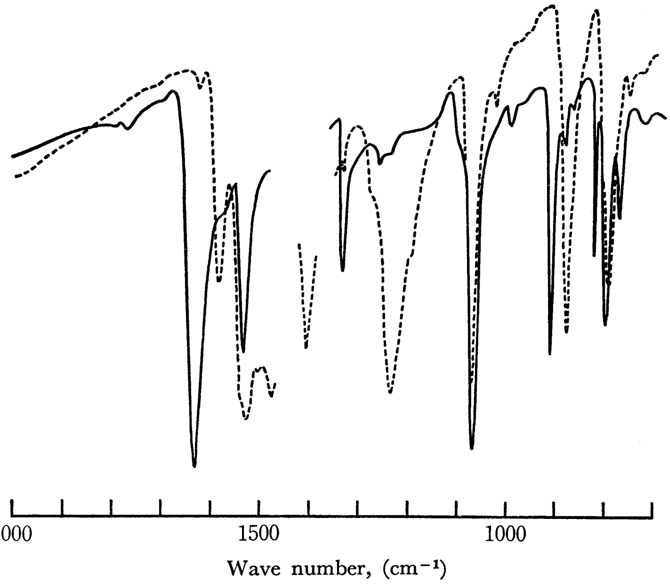

Fig. 8. Vibrational spectra of TCDQ (——) and Na$^+$TCDQ$^-$ (----).

The spectrum of the complex ethyldi-n-propylammonium TCDQ salt bears some resemblance to the spectrum of TCDQ and also that of the semiquinone salt. That is, the presence of bands at 1410, 1250, and 880 cm^{-1} is characteristic of the semiquinone ion. On the other hand, the triplet around 800 cm^{-1} may be ascribed to the original quinone. However, no strong broad band to be assigned to the carbonyl stretching vibration is observed at the wavenumber

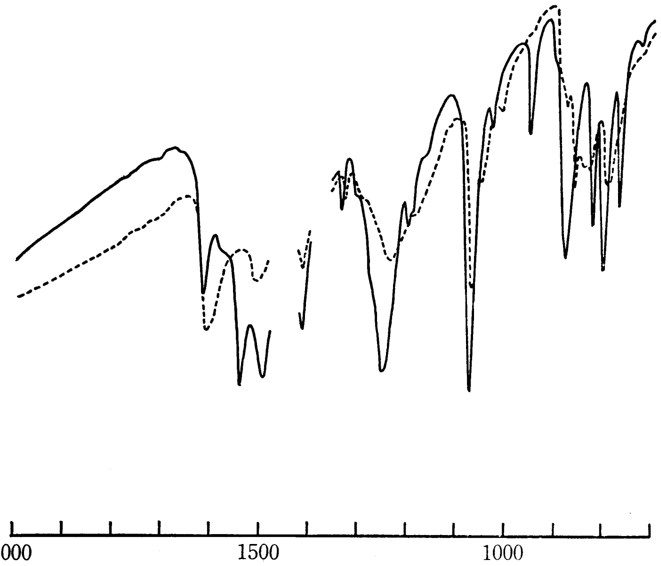

Fig. 9. Vibrational spectra of the complex TCDQ salts containing ethyldi-n-propylammonium ion (——) and cobalticinium ion (----).

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[35] Y. Iida, *ibid.*, **43**, 2772 (1970).

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

[37] G. B. Bonino and E. Scrocco, *Atti Accad. Naz. Lincei, Rend. Classe Sci. Fis. Mat. e Nat.*, **6**, 421 (1949).

[38] G. Berthier, B. Pullman, and J. Pontis, *J. Chim. Phys.*, **49**, 367 (1952).

[39] W. Kemula and M. T. Krygowski, *Bull. Acad. Pol. Sci., Sér. Sci. Chim.*, **15**, 479 (1967).

[40] Y. Iida, This Bulletin, **43**, 345 (1970).

corresponding to either that in the quinone or that in the semiquinone ion. A rather narrow band appears at 1610 cm^{-1}. The complex TCDQ salts of di-*n*-propyl-ammonium and methyldi-*n*-propylammonium show spectra similar to this. The spectra of most of the complex TCDQ salts are different from those mentioned above. For example, the spectrum of the cobalticinium salt is shown in Fig. 9. Bands at 860, 1010, and 1410 cm^{-1} form the spectrum of the cation. Here again, we see neither the pattern due to the quinone molecule nor that due to the semiquinone ion. A single broad carbonyl band appears at 1610 cm^{-1}. This wavenumber is intermediate between that in the the quinone, 1640 cm^{-1}, and that in the semiquinone salt, 1530 cm^{-1}. On the basis of this observation, we may conclude that the negative charge is equally shared by the two molecules of the quinone. If so, the quinone molecules in the afore-mentioned three ammonium salts may not be exactly equivalent to each other. The resistivity values seem to have no direct relation with the type of the vibrational spectrum, for the highest value among the complex TCDQ salts is 2×10^5 ohm cm in the quinolinium salt, and the lowest, 24 ohm cm in the ferricinium salt. Their spectra are all of the same type. In all the complexs TCDQ salt, the carbonyl stretching-vibration band is found in the range from 1605 to 1625 cm^{-1} regardless of the composition. This is rather surprising because the formal change per quinone molecule is a half in the 1 : 2 salt and two-thirds in the 2 : 3 salt. Actually, rough estimates derived from a comparison of the red shift of the carbonyl mode in the complex salts with the shift found in the sodium salt are no larger than one-third. The location of the band appearing at 1070 cm^{-1}, in the quinone is hardly affected by the reduction; however, a splitting of as much as 10—25 cm^{-1} is observed in the salts containing some ammonium ions and mostly heterocyclic cations.

The spectrum of TBDQ has a strong carbonyl band at 1630 cm^{-1}. In the simple salts, this band is shifted to the low-energy side by 80—100 cm^{-1}, depending upon the kind of cation. Figure 10 presents the spectra of the simple and complex *N*-methyl-acridinium salts. Here, the carbonyl stretching bands are found at 1545 and 1595 cm^{-1} respectively. The strong broad band located around 1250 cm^{-1} is characteristic of the salts, and it is not observed before the reduction. In the other complex TBDQ salts, the band due to carbonyl stretching appears in the range from 1595 to 1615 cm^{-1}, again regardless of the composition. As in the series of the TCDQ salts, this band is rather weak and narrow in some ammonium salts. Although the band located at 1020 cm^{-1} in the spectra of Fig. 10 apparently corresponds to the 1070 cm^{-1} band in TCDQ, no splitting is observed in any complex TBDQ salts.

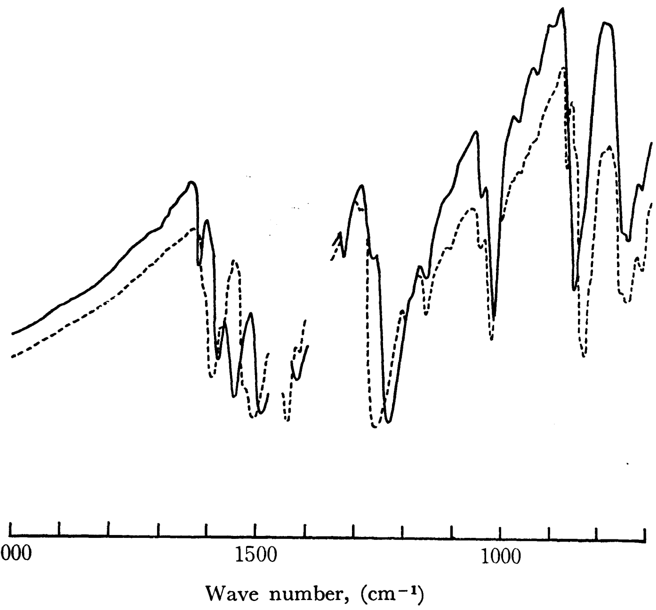

Fig. 10. Vibrational spectra of *N*-methyl-acridinium-TBDQ, the simple salt (——) and the complex salt (----).

Lastly, we wish to emphasize that quinones, if suitably selected, can form series of complex anion-radical salts with various onium cations as well as TCNQ does. Work to prepare a new series of complex anion-radical salts is now in progress using 2,3-dicyano-1,4-naphthoquinone.

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