BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 637—643 (1969)

Electronic Spectra of Crystalline TCNQ Anion Radical Salts. II. Complex Salts*[1]

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(Received July 17, 1968)

The present paper deals with crystalline TCNQ anion radical "complex" salts of $(M^+)_2(TCNQ)_3^{\bar{}\bar{}}$ and $M^+(TCNQ)_2^{\bar{}}$ composed of the formally-neutral TCNQ and its anion radical $TCNQ^{\bar{}}$ Their crystalline electronic spectra were measured in the range between 4.0 and 30.8 kK by diffuse reflectance and in the 0.65—4.0 kK range by transmittance. None of their spectra except those of the (2 : 3) compounds were found to bear any resemblance to those in the simple salts. Although the spectra of the (2 : 3) compounds are similar to those of the simple salts with low conductivities, the former exhibit an additional weak absorption in the range lower than 6 kK. The (1 : 2) compounds with intermediate conductivities show a strong band around 3 kK, and those with high conductivities, around 2.0—2.5 kK. Their spectra are discussed on the basis of the interaction among unpaired electrons in connection with their electrical and magnetic properties. The difference in the interaction modes of the ion radicals between "simple" and "complex" salts is also speculated upon.

Our primary interest is in studying the interactions among unpaired electrons in the solid state of ion radical salts. Along this line, we have investigated the crystalline electronic spectra of Würster's cation radical salts[1)] and 7,7,8,8-tetracyanoquinodimethane (TCNQ) anion radical simple salts.[2)] It has been concluded that their crystalline spectra arise from charge-transfer interaction between ion radicals. Furthermore, the spectra have been proved to have a close correlation with their electrical and magnetic properties. In TCNQ simple salts, the charge-transfer bands have been observed around 9 kK in low-conductivity compounds and at 4.3 kK in high-conductivity compounds. On the other hand, TCNQ forms new classes of complex salts of $(M^+)_2(TCNQ)_3^{\bar{}\bar{}}$ and $M^+(TCNQ)_2^{\bar{}}$ as well as simple salts of $M^+TCNQ^{\bar{}}$, where M^+ represents a diamagnetic counter cation.[3,4)] Thus, the complex salts include the formally-neutral TCNQ besides the anion radical $TCNQ^{\bar{}}$. The complex salts range from semimetal-like substances with a temperature-independent paramagnetism to intermediate-conductivity compounds with triplet-exciton systems.[3-8)] The purpose of the present paper is to study the electronic states of the complex salts in the solid state by means of their crystalline electronic spectra. This study also involves the effects of the introduction of neutral TCNQ molecules on the modes of the interaction among unpaired electrons previously investigated in the simple salts.[2)]

Experimental

Materials. The TCNQ complex salts under investigation are classified below.

The (2 : 3) Compounds. $(Cs^+)_2(TCNQ)_3^{\bar{}\bar{}}$ and $(Morpholinium^+)_2(TCNQ)_3^{\bar{}\bar{}}$.

The (1 : 2) Compounds with Intermediate Conductivity. Methyltriphenylphosphonium$^+(TCNQ)_2^{\bar{}}$, Methyltriphenylarsonium$^+(TCNQ)_2^{\bar{}}$, Ethyltriphenylphosphonium$^+(TCNQ)_2^{\bar{}}$, Ethyltriphenylarsonium$^+(TCNQ)_2^{\bar{}}$, Trimethylphenylammonium$^+(TCNQ)_2^{\bar{}}$, Triethylammonium$^+(TCNQ)_2^{\bar{}}$, Triethylphenylammonium$^+(TCNQ)_2^{\bar{}}$, Tetraethylammonium$^+(TCNQ)_2^{\bar{}}$, Ethyltri-*n*-propylammonium$^+(TCNQ)_2^{\bar{}}$, and Tetra-*n*-propylammonium$^+(TCNQ)_2^{\bar{}}$.

The (1 : 2) Compounds with High Conductivity. Quinolinium$^+(TCNQ)_2^{\bar{}}$, *N*-Methylquinolinium$^+(TCNQ)_2^{\bar{}}$, *N*-Ethylquinolinium$^+(TCNQ)_2^{\bar{}}$, *N*-(*n*-Propyl)quinolinium$^+$

[*1] Presented in part at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967, and at the Symposium on Molecular Structure, Sapporo, October, 1967.

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

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

3) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).

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

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

6) D. B. Chesnut and W. D. Phillips, *ibid.*, **35**, 1002 (1961).

7) D. B. Chesnut and P. Arthur, Jr., *ibid.*, **36**, 2969 (1962).

8) M. T. Jones and D. B. Chesnut, *ibid.*, **38**, 1311 (1963).

$(\mathrm{TCNQ})_2^{-}$, *N*-Methylisoquinolinium$^+(\mathrm{TCNQ})_2^{-}$, *N*-Ethylisoquinolinium$^+(\mathrm{TCNQ})_2^{-}$, Quinaldinium$^+(\mathrm{TCNQ})_2^{-}$, *N*-Methylquinaldinium$^+(\mathrm{TCNQ})_2^{-}$, *N*-Ethylquinaldinium$^+(\mathrm{TCNQ})_2^{-}$, Lepidinium$^+(\mathrm{TCNQ})_2^{-}$, *N*-Methyllepidinium$^+(\mathrm{TCNQ})_2^{-}$, *N*-Ethyl-2,6-dimethylquinolinium$^+(\mathrm{TCNQ})_2^{-}$, and *N*-Methylacridinium$^+$ $(\mathrm{TCNQ})_2^{-}$.

These compounds were prepared by a direct reaction between TCNQ and the iodides in acetonitrile.[3] The compositions of the compounds, which have not yet appeared in the literature, were determined on the basis of the intensity-ratios of some absorption bands measured in acetonitrile.[3]

Measurements. The measurements of the absorption spectra in acetonitrile were carried out under the conditions presented in a previous paper.[2] The crystalline electronic spectra were measured in the range between 4.0 and 30.8 kK by means of diffuse reflectance and were plotted using the Kubelka-Munk equation $f(R)=(1-R)^2/2R$, where R is the reflectance. The details were the same as in previous papers.[1,2] The absorption spectra in the solid state were recorded in the range between 0.65 and 4.0 kK as Nujol mulls.

Results and Discussion

The absorption spectra of neutral TCNQ and anion radical TCNQ^{-} in acetonitrile have been illustrated in a previous paper.[2] As for the complex salts in acetonitrile, the components have been found to be completely dissociated, thus giving a spectra consisting of those of independent TCNQ and TCNQ^{-} molecules. However, in the solid state, TCNQ molecules form "supermolecules" composed of their unique groups.[4-9]

These complex salts may be divided into (2 : 3) and (1 : 2) salts on the basis of the ratio of cations to TCNQ molecules. It is further possible to divide the (1 : 2) salts into intermediate- and high-conductivity compounds on the basis of their electrical properties.[4] These classifications allow correlation with the optical and magnetic properties in the complex salts to be discussed below.

The (2 : 3) Compounds. They are restricted to $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3^{--}$ and $(\mathrm{Morpholinium}^+)_2$-$(\mathrm{TCNQ})_3^{--}$, which were obtained in the form of large blue-black crystals. They have conductivities of the order of 10^{-3}—$10^{-5}\Omega^{-1}\,\mathrm{cm}^{-1}$ or less and activation energies as high as 0.3 eV.[3,4]

$(Cs^+)_2(TCNQ)_3^{--}$. According to Fritchie and Arthur,[9] this salt crystallizes with the symmetry of the space group $P2_1/c(C_{2h}{}^5)$ and with two formula units per cell. TCNQ molecules pack face-to-face to form somewhat irregular columns parallel to the b-axis, with a unique grouping of charge-transfer-bonded triads. The inter-planar spacing is 3.22 Å within a triad and 3.26 Å between triads.

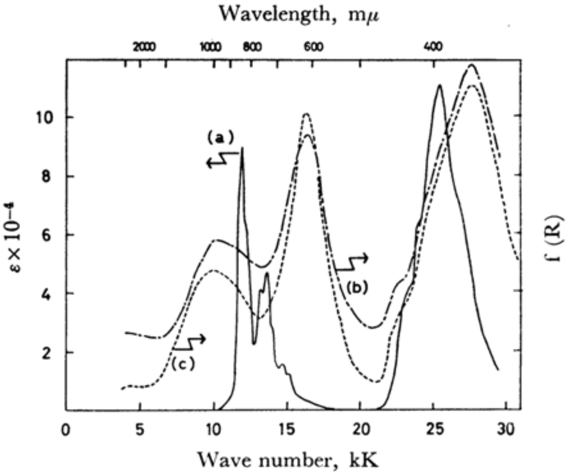

Fig. 1. Electronic spectra of $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3^{--}$ in acetonitrile solution (a), $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3^{--}$ in the solid state (b) and $(\mathrm{Morpholinium}^+)_2(\mathrm{TCNQ})_3^{--}$ in the solid state (c).

The absorption spectrum of the salt in acetonitrile is shown in Fig. 1, curve a. The crystalline spectrum illustrated in Fig. 1, curve b, is found to resemble that of the TCNQ^{-} dimer in an aqueous solution[10] or those of the simple salts with low-conductivities.[2] The crystalline spectrum of the Cs salt comprises peaks at 10.1, 16.2 and 27.5 kK, a weak band in the region less than 6 kK and extending to 4 kK, and a slight shoulder around 23 kK. These three peaks almost correspond to those at 8.5, 16.4, and 27.8 kK respectively in the simple potassium salt.[2] The high-energy peaks at 16.2 and 27.5 kK in the Cs salt may also well be compared with those at 15.6 and 27.0 kK respectively in the dimer.[10] Neutral TCNQ in acetonitrile has a band peak at 25.3 kK with a molar extinction coefficient as high as 65000,[2] therefore, if this band makes some contribution to the band at 27.5 kK in the Cs salt, the appearance of a shoulder or a remarkable increase in the intensity relative to that at 16.2 kK may be expected. However, the spectrum of the Cs salt shows that this appears not to be the case. The shoulder around 23 kK is too slight to be the expected one; it is probably due to a non-interacting TCNQ or TCNQ^{-} monomer in some kind of defects. Thus, the band due to TCNQ may be regarded as appreciably blue-shifted, thus making only a small contribution to the band at 27.5 kK. Therefore, for the same reason as with the simple salts,[2] the bands at 16.2 and 27.5 kK in the Cs salt should mainly be assigned to the shifted bands of the TCNQ^{-} monomer, while the band at 10.1 kK must be the charge-transfer band between TCNQ^{-} molecules (*cf.* Ref. 11). Finally, the weak low-energy band characteristic of the (2 : 3) salts may be regarded as due to charge-transfer interaction between TCNQ^{-} and

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[9] C. J. Fritchie, Jr., and P. Arthur, Jr., *Acta Cryst.*, **21**, 139 (1966).

[10] R. H. Boyd and W. D. Phillips, *J. Chem. Phys.*, **43**, 2927 (1965).

TCNQ, for it appears only upon the introduction of TCNQ.

The finding that the crystalline spectrum is due almost entirely to the pair-by-pair interaction between unpaired electrons in the Cs salt is probably associated with its magnetic properties. According to Chesnut and Arthur,[7] its paramagnetism is to be attributed to a triplet-exciton state lying 0.16 eV above a singlet state.[8] Understandably, the pair-by-pair interaction leads to the singlet-triplet energy separation. However, the addition of neutral TCNQ to the TCNQ$^{\cdot-}$ dimer may contribute to a reduction of the localized triplet character, producing a triplet exciton in the crystal. The reason for this is as follows. With respect to the unpaired electrons, the dimer in the (2 : 3) salt corresponds to the doubly-charged TCNQ triad. The interacting distance between two unpaired electrons in the triplet state of the triad may be longer than that in the dimer without neutral TCNQ, because the lowest-triplet configuration is not mixed with the charge-transfer configuration and, consequently, the two electrons in the triplet state may be regarded as mutually repulsive.[2,11] Thus, the introduction of neutral TCNQ should decrease the intra-dimer interaction and increase the inter-dimer interaction in the triplet state, at least to some extent, thus resulting in the triplet exciton. On the other hand, the electronic transitions conceived here occur among singlet states, where the mixing of the lowest singlet configuration with the charge-transfer configuration in the triad is quite significant. Therefore, the pair-by-pair interaction may be regarded as strong in the singlet states, giving rise to the spectral resemblance to the dimer without neutral TCNQ. At any rate, the presence of additional TCNQ to this salt seems to perturb weakly the pair-by-pair interaction of ion radicals. This effect may make a small contribution to the increase in electrical conductivity. The conductivity of the complex Cs salt ($1\times10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}$ at 23°C, compaction measurement) should be compared with that of the simple salt with the same cation (5×10^{-4}).[4]

(Morpholinium⁺)₂(TCNQ)₃$^{\cdot-}$. The crystalline spectrum (Fig. 1, curve c) consists of peaks at 10.0, 16.3, and 27.6 kK, and a weak band in the region from less than 6 kK to 4 kK. These bands agree well with the corresponding bands in the Cs salt. Furthermore, the spectrum of the complex morpholinium salt bears a close resemblance, except the weak low-energy band, to that in the simple salt with the same cation,[2] which has peaks at 9.5, 16.3, and 27.7 kK. The band at 9.5 kK in the simple salt has been ascribed to the inter-radical charge-transfer transition, to which the band at 10.0 kK in the complex salt is also regarded as due. Again, in these morpholinium salts, the weak low-energy band is also characteristic of the complex salt. Although the electrical conductivity of the complex salt ($2\times10^{-4}\ \Omega^{-1}\text{cm}^{-1}$, single-crystal measurement)[3] is larger than that of the simple salt (1×10^{-9}),[4] the former is classified as part of the group with intermediate conductivity. Accordingly, the perturbation due to the introduction of TCNQ is certainly weak. There are many reasons to believe that the complex morpholinium salt possesses a crystal structure similar to that of the Cs salt and exhibits magnetic properties based on a triplet exciton.[6]

The (1 : 2) Intermediate-Conductivity Compounds. The counter cations of these compounds, such as methyltriphenylphosphonium (Ph_3PCH_3) or methyltriphenylarsonium (Ph_3AsCH_3), usually have a nearly spherical form and a relatively large size. These salts are obtained in the form of well-developed blue-black crystals. They have conductivities of the order of $10^{-2}\ \Omega^{-1}\ \text{cm}^{-1}$ or less, and activation energies as high as 0.3 eV.[3,4] In the following paragraphs, the results of some representative samples will be discussed in detail.

$(Ph_3XCH_3)^+(TCNQ)_2^{\cdot-}$ (X=P or As). These salts have almost identical electronic properties except for the occurrence of a phase transition in the phosphonium salt at 40°C.*2 The crystal structures of these salts have not yet been ascertained. The absorption spectrum of the phosphonium salt in acetonitrile and its crystalline spectrum are given

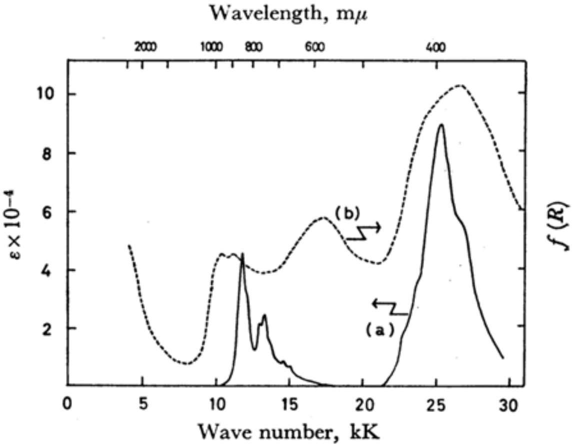

Fig. 2. Electronic spectra of $(\text{Ph}_3\text{PCH}_3)^+(\text{TCNQ})_2^{\cdot-}$ in acetonitrile solution (a) and in the solid state (b).

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[11] K. H. Hausser and J. N. Murrell, *ibid.*, **27**, 500 (1957).

*2 In the phosphonium salt, a phase transition occurs at 40°C, where an abrupt and reversible change in ESR intensity and electrical conductivity has been observed. The measurement of the thermal analysis has also been carried out. See Y. Iida, M. Kinoshita, M. Sano and H. Akamatu, This Bulletin, **37**, 428 (1964); Y. Iida, M. Kinoshita, A. Kawamori and K. Suzuki, *ibid.*, **37**, 764 (1964).

in Fig. 2 by curve a and curve b respectively. Quite similar electronic spectra in acetonitrile and in the solid state were obtained in the arsonium salt. The crystalline spectrum of the phosphonium or the arsonium salt, on the other hand, bears no resemblance to the dimer spectrum, consisting of peaks at 10.4, 11.4, 17.2, and 26.3 kK, and an intense band with its peak in the region less than 4 kK. Although the locations of the bands at 17.2 and 26.3 kK nearly correspond to those at 15.6 and 27.0 kK respectively in the dimer,10) the band at 26.3 kK should comprise not only that due to the dimer but also that due to neutral TCNQ, because the band at 26.3 kK has an appreciably larger intensity than that at 17.2 kK and even has its shoulder around 24 kK. There has been no contribution of the band due to TCNQ in the (2 : 3) salts. The pair-by-pair interaction as to the unpaired electrons in the phosphonium or the arsonium salt is decreased compared to that in the (2 : 3) salts, but it still remains, because the peak at 17.2 kK almost certainly to be ascribed to the dimer spectrum10) is relatively diffused and continuously overlaps with other bands. The decrease is probably caused by the presence of more TCNQ in the (1 : 2) salt than in the (2 : 3) salt. Whether the doublet bands at 10.4 and 11.4 kK are due to two different electronic transitions or to one with vibrational structures is not clear. Furthermore, it is difficult to decide whether they are shifted bands of the $TCNQ^{\overline{\cdot}}$ monomer or charge-transfer bands between $TCNQ^{\overline{\cdot}}$ molecules. However, it can be said that, although the charge-transfer band is expected to appear around 10 kK, the band splitting may make the latter possibility improbable. On the other hand, the location of the band peak in the range less than 4 kK was not determined by the diffuse reflectance spectrum. Therefore, we examined the infrared absorption spectrum, which indicates that this intense electronic band partially screens the vibrational spectrum and has its peak around 2.9—3.3 kK. It is not clear whether this band is to be ascribed to the charge-transfer band between $TCNQ^{\overline{\cdot}}$ and TCNQ, or to the direct transition from the valence state to the electrical conduction state. Possible support for the former possibility is that similar low-energy bands, although weak in intensity, have been observed in the (2 : 3) salts and that, here, they are remarkably increased in intensity by the further introduction of TCNQ. However, they appear in the compounds with relatively high electrical conductivities. Therefore, we believe that they are closely correlated with their high conductivities.

The paramagnetism of the phosphonium or the arsonium salt is based on a triplet-exciton state lying 0.062 eV above the singlet state.6) Therefore, the mode of interaction among the ion radicals is certainly by pairs. However, the delocalization of the triplet exciton in these salts is increased (*i. e.*, there is an increase in the triplet-exciton band width) and its singlet-triplet energy separation is decreased, compared with the values in the Cs salt.12) This change can probably be said to be caused, by an extension of the reason mentioned above for the Cs salt, by the presence of the additional TCNQ. However, in these (1 : 2) salts, the presence of this TCNQ still appreciably modifies the crystalline electronic spectrum with a pair-by-pair character. Such was not the case with the (2 : 3) salts, where the change is relatively slight. Furthermore, the presence of neutral TCNQ in the (1 : 2) salts causes a remarkable increase in the electrical conductivity. For example, the complex phosphonium salt has $2\times10^{-2}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ at 23°C (single-crystal measurement), a value which is markedly larger than the 2×10^{-11} of the simple salt with the same cation.4) The former should also be compared with the 1×10^{-3} value of the complex Cs salt (single-crystal measurement),4) where, on the contrary, the effect has been regarded as weak.

It may be concluded that, in the phosphonium or the arsonium salt, the perturbation due to the introduction of TCNQ is relatively strong. Nonetheless, one can still picture the TCNQ molecules as existing in unique groups of four (*i. e.*, two $TCNQ^{\overline{\cdot}}$ and two TCNQ molecules) along a one-dimensional column in the solid state.

The Other Compounds. All of the other compounds belonging to this group bear, more or less, an optical resemblance to those of the phosphonium or the arsonium salt. The band peaks of their crystalline spectra are designated as shown in Fig. 3, which also gives an example of the spectrum of

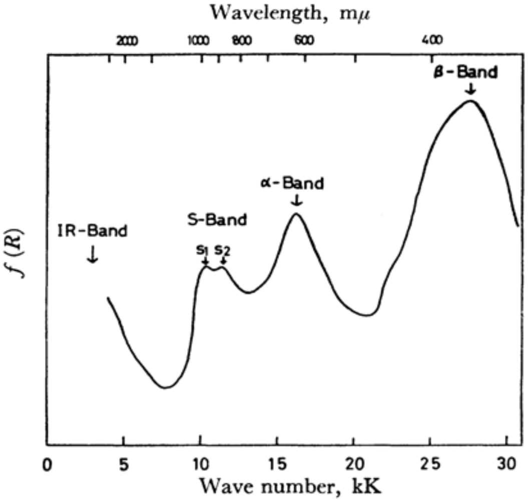

Fig. 3. Electronic spectrum of $Triethylammonium^{+}$-$(TCNQ)_2^{\overline{\cdot}}$ in the solid state, together with the designation of its band peaks.

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12) Z. G. Soos and R. C. Hughes, *J. Chem. Phys.*, **46**, 253 (1967).

the triethylammonium salt. The features of the low-energy band (IR-band), the splitting (~1 kK) of the doublet S_1- and S_2-bands, and the rather sharp α-band relative to the (1 : 2) high-conductivity compounds (see below) should be noted. The locations of the IR-bands in these intermediate-conductivity compounds are estimated to be in the same range as in the phosphonium salt (*i. e.*, 2.9–3.3 kK). The other peaks are listed in Table 1. Evidently, the corresponding band peaks are shifted slightly by the change in the cations; on this change, however, depends the sharpness of the α-bands related to the degree of pair-by-pair interaction of ion radicals. The triethylammonium salt is found to have an especially sharp and strong α-band, exhibiting, on the other hand, magnetic properties based on a triplet exciton.*3

TABLE 1. THE DATA FOR THE BAND PEAKS EXCEPT THE IR-BAND IN THE CRYSTALLINE ELECTRONIC SPECTRA OF THE (1 : 2) INTERMEDIATE-CONDUCTIVITY TCNQ COMPLEX SALTS

Cation*	S-Band(kK) S_1	S-Band(kK) S_2	α-Band (kK)	β-Band (kK)
$MePh_3P$	10.4	11.4	17.2	26.3
$MePh_3As$	10.3	11.4	17.2	26.7
$EtPh_3P$	11.3		17.2	27.0
$EtPh_3As$	11.3		16.9	26.7
Me_3PhN	10.2	11.5	16.4	26.3
Et_3HN	10.3	11.4	16.4	27.2
Et_3PhN	10.5	11.4	16.0	27.5
Et_4N	10.0	11.4	17.0	27.2
Et(*n*-Pro)$_3$N	9.9	11.3	16.3	26.7
n-Pro$_4$N	9.9	11.3	16.3	27.0

* Substituents of methyl, ethyl, *n*-propyl and phenyl are abbreviated as Me, Et, *n*-Pro and Ph, respectively.

In all events, in the (1 : 2) intermediate-conductivity compounds, the pair-by-pair interaction of ion radicals is relatively decreased by the further introduction of TCNQ. However, we believe that that interaction mode will still not be changed.

The (1:2) High-Conductivity Compounds. The counter cations of these compounds are aromatic or heterocyclic cations such as quinolinium. These compounds come out of the solution in the form of small blue-black needles. The quinolinium salt, for example, exhibits an electrical conductivity as high as 100 $\Omega^{-1}\,cm^{-1}$ and an activation energy as low as 0.03 eV (single-crystal measurement).[4] In the following paragraphs, the results of the crystalline spectra in some representative samples will be discussed in detail.

Quinolinium$^+$(*TCNQ*)$_2^{\cdot-}$. The crystal structure of this salt has not yet been ascertained. The absorption spectrum in acetonitrile, shown by curve a of Fig. 4, is essentially the same as those of the (1 : 2) intermediate-conductivity compounds. Although the crystalline spectrum illustrated by curve b of Fig. 4 bears a rough resemblance to those of the intermediate-conductivity compounds, some differences may be noted. The crystalline spectrum of the quinolinium salt has peaks at 10.5, 17.4, and 26.7 kK, and an intense band with its peak in the range less than 4 kK. The last band peak was not determined by means of the diffuse reflectance, so we have also examined the absorption spectrum, which shows, in this case, that the vibrational spectrum is completely screened by this intense electronic transition. The location of the peak is thus estimated to be around 2.0–2.5 kK. This band may be connected with that observed in the far infrared region by Kondow *et al.*[13] It should also be mentioned that this band is not exactly the same as the IR-band in the intermediate-conductivity compounds, which is around 2.9–3.3 kK. In connection with the contrast of their conductivities, this difference in their lowest-energy bands implies a difference in the interaction modes of unpaired electrons between high- and intermediate-conductivity compounds (see below). Furthermore, there is reason to believe that these bands in both the groups may arise from a transition from the valence band to the electrical conduction band.[13]

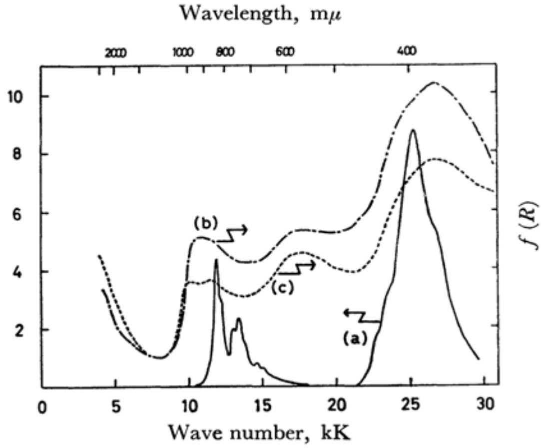

Fig. 4. Electronic spectra of Quinolinium$^+$ (TCNQ)$_2^{\cdot-}$ in acetonitrile solution (a), Quinolinium$^+$ (TCNQ)$_2^{\cdot-}$ in the solid state (b) and *N*-(*n*-Propyl)quinolinium$^+$ (TCNQ)$_2^{\cdot-}$ in the solid state (c).

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*3 In explaining the temperature dependence of the magnetic susceptibility of the triethylammonium salt, Soos and Hughes' theory (see Ref. 12) has supported the model of a weakly alternating antiferromagnet rather than that of almost isolated triplets. However, in the crystalline spectrum presented here, the especially sharp and strong α-band may imply a strongly pair-by-pair interaction of ion radicals in this salt.

Table 2. The data for the band peaks except the lowest-energy band in the crystalline electronic spectra of the (1 : 2) high-conductivity TCNQ complex salts. The designation of the bands nearly corresponds to that in Fig. 3

Cation	S-Band (kK)		α-Band (kK)	β-Band (kK)
	S_1	S_2		
Quinolinium	10.5		17.4	26.7
N-Methylquinolinium	10.2	11.4	16.3	27.4
N-Ethylquinolinium	10.0	11.6	16.9	26.7
N-(*n*-Propyl)quinolinium	10.0	11.6	17.8	26.7
N-Methylisoquinolinium	10.4	11.4	18.2	25.8
N-Ethylisoquinolinium	10.3	11.6	16.3	—
Quinaldinium	10.5		17.7	26.3
N-Methylquinaldinium	10.7		17.8	27.5
N-Ethylquinaldinium	10.2	11.6	16.1	27.0
Lepidinium	12.0		17.5	26.3
N-Methyllepidinium	10.0	11.4	16.4	27.0
N-Ethyl-2,6-dimethylquinolinium	10.4	11.8	18.0	—
N-Methylacridinium	11.2		17.8	27.5

The quinolinium salt has one band, around 10.5 kK, corresponding to the S_1- and S_2-bands in the intermediate-conductivity compounds. Usually, the spectra of the compounds with high conductivities are found to comprise one band with no such splitting, whereas the splitting tends to appear with a decrease in the conductivity. Accordingly, the nature of the band at 10.5 kK depends on its conductivity. However, its origin is not clear. The band at 17.4 kK, probably related to the pair-by-pair interaction of ion radicals, is more diffused than the α-band in the intermediate-conductivity compounds and is remarkably overlapped with other bands. These findings imply that the pair-by-pair interaction would almost vanish in the quinolinium salt. On the other hand, the band around 26.7 kK rather resembles the β-band in the intermediate-conductivity compounds. These observations provide us with some reasons for the more-than-pair-by-pair interaction of ion radicals in this salt. As in the cases with some TCNQ salts,[7,9,14,15] the TCNQ molecules in the quinolinium salt should form a one-dimensional column, so each unpaired electron should interact equally and strongly with two neighbors. In this respect, the (1 : 2) high-conductivity compounds are different from the (1 : 2) intermediate-conductivity compounds. The more-than-pair-by-pair interaction of the ion radicals in the quinolinium salt causes the delocalization of the unpaired electrons, which, in turn, brings about its high electrical conductivity and the low activation energy. Also, in this case, the presence of neutral TCNQ makes some contribution to the delocalization. The mode of the interaction is, except for the exclusion of the neutral molecules, similar to those of some Würster's salts with a more-than-pair-by-pair and strong interaction[1] or that of the high-conductivity TCNQ simple salt of *N*-methylphenazinium.[2] In view of these facts, we believe that the magnetic property of the quinolinium salt with an almost temperature-independent paramagnetism ($\chi=4.3\pm0.2\times10^{-7}$ emu/g)[5] may be based on a non-alternating linear chain antiferromagnet. However, we hesitate to accept the idea of a complete Heisenberg antiferromagnet because of the delocalization of the unpaired electrons.

The Other Compounds. All the other compounds belonging to this group show crystalline spectra essentially like that of the quinolinium salt. However, it is noteworthy that a splitting of the doublet bands around 10 kK appears, and that the sharpness of the band around 17 kK is increased, with a decrease in their electrical conductivities. The band peaks of their crystalline spectra, nearly corresponding to S-, α-, and β-bands in the intermediate-conductivity compounds, are listed in Table 2. The spectrum of the *N*-(*n*-propyl)quinolinium salt, as an example, is illustrated by curve c of Fig. 4. The decrease in the conductivities depends largely on the size and the shape of the cations. For example, the introduction of a substituent as bulky as *n*-propyl to the quinolinium cation decreases 100 Ω^{-1} cm^{-1} at 23°C of the quinolinium salt[4] to 2 of the *N*-(*n*-propyl)quinolinium salt.[3] Therefore, the introduction of bulky substituents to the flat cations (*e. g.*, aromatic or heterocyclic) leads to intermediate conductivities,

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13) T. Kondow, K. Siratori and H. Inokuchi, *J. Phys. Soc. Japan*, **21**, 824 (1966); **23**, 98 (1967).

14) G. R. Anderson and C. J. Fritchie, Jr., Second National Meeting, Society for Applied Spectroscopy, San Diego, October 14, Paper 111 (1963).

15) C. J. Fritchie, Jr., *Acta Cryst.*, **20**, 892 (1966).

and the doublet bands around 10 kK and a rather sharp and strong α-band come to be clearly observed. Accordingly, it may be concluded that those introductions of substituents contribute, to varying degrees, to the change of the more-than-pair-by-pair interaction of ion radicals into the pair-by-pair interaction. It is expected that this change in the interaction modes will greatly affect their magnetic properties, again producing triplet excitons.

The author wishes to express his thanks to Professor Yoshio Matsunaga for his generous support to this work and to Mr. Nobuhiko Miyajima for his technical assistance.