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Electronic Spectra of Crystalline TCNQ Anion Radical Salts. I. Simple Salts*1

Yôichi IIDA

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

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The present paper deals with crystalline TCNQ anion radical "simple" salts of M^+ $TCNQ^-$, where M^+ represents a diamagnetic counter cation. Their crystalline electronic spectra were measured in the range between 4.0 and 30.8 kK by means of diffuse reflectance. The crystalline spectra thus obtained were quite different from that of the TCNQ radical anion monomer and exhibited a broad and intense low-energy band around 9 kK in the low-conductivity compounds and at 4.3 kK in the high-conductivity compound. These bands were ascribed to inter-radical charge-transfer in the solid state. The crystalline spectra were found to be closely correlated to their unusual electrical and magnetic properties. It was concluded that these physical properties were based on a unique TCNQ molecular arrangement in groups of several or an infinite number of face-to-face molecular systems.

In a previous paper,[1] it has been shown that Würster's salts exhibit characteristic electronic and magnetic properties in the solid state. These properties result from charge-transfer interaction between the cation radicals. Unusual low-energy bands in the diffuse reflectance spectra have been identified as inter-radical charge-transfer bands. In connection with them, the magnetic properties of the salts have been speculated on on the basis of antiferromagnetic interaction between ion radicals. Charge-transfer interaction might make a significant contribution to the stabilization of the antiferromagnetic interaction.

However, these interesting physical properties may not be restricted to Würster's salts, but may be regarded as of the nature of ion (cation and anion) radical salts. In ion radical salts, the unpaired electrons play a predominant role in causing these properties. Along this line, measurements of the magnetic susceptibility and ESR have been powerful tools for clarifying the solid-state interactions among unpaired electrons.[2-8] However, the study of the crystalline electronic spectra may still provide us with useful information concerning these interaction mechanisms. With this hope, we will deal with the anion radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ).[9] TCNQ is a well-known strong electron acceptor which forms stable crystalline anion radical "simple" salts of the M^+ $TCNQ^-$ type and new classes of "complex" salts of $(M^+)_2(TCNQ)_3^{--}$ and $M^+(TCNQ)_2^-$, which contain the formally neutral TCNQ and the anion radical $TCNQ^-$. The advantage in dealing with TCNQ salts is that their salts are easily obtained as stable single crystals and that, consequently, their electrical and magnetic properties have been extensively studied.[5-11] Thus, their crystalline electronic spectra can be studied in connection with these properties. The purpose of the present paper is to clarify the crystalline electronic spectra of TCNQ anion radical simple salts by means of diffuse reflectance and to discuss the solid-state interactions among unpaired electrons.

Experimental

Materials. The ten TCNQ simple salts under investigation are Li^+TCNQ^-, Na^+TCNQ^-, K^+TCNQ^-, NH_4^+ $TCNQ^-$, Triethylammonium$^+$ $TCNQ^-$, Methyltriphenylphosphonium$^+TCNQ^-$, Methyltriphenylarsonium$^+TCNQ^-$, Morpholinium$^+TCNQ^-$, *N*-Methylquinolinium$^+TCNQ^-$, and *N*-Methylphenazinium$^+TCNQ^-$.

Li^+TCNQ^-, Na^+TCNQ^-, K^+TCNQ^-, NH_4^+ $TCNQ^-$, and Morpholinium$^+TCNQ^-$ were prepared

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by a direct reaction between TCNQ and the iodides in acetonitrile.[9] The other compounds were prepared by the metatheses of the corresponding cation sources with Li^+TCNQ^-.[9,11]

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

The crystalline electronic spectra were measured in the range between 4.0 and 30.8 kK by means of diffuse reflectance at room temperature. The electronic absorption spectra were reproduced employing the Kubelka-Munk function $f(R)=(1-R)^2/2R$, where R is the reflectance. The experimental details are the same as those described in a previous paper.[1] Potassium bromide, sodium chloride, and naphthalene were used as solid diluents and also as references.

Results and Discussion

The absorption spectra of neutral TCNQ and anion radical $TCNQ^-$ in acetonitrile are illustrated in Fig. 1, Curve a and Curve b respectively. The absorption spectrum of TCNQ has a peak at 25.3 kK with a molar extinction coefficient (ε) of 65000, while that of $TCNQ^-$ shows $\varepsilon=21500$ at 25.3 kK and $\varepsilon=45000$ at 11.9 kK. The natures of these absorption bands have been investigated by Lowitz by the molecular orbital method.[12] The reversible dimerization of $TCNQ^-$ in an aqueous solution has been noted by Boyd and Phillips.[13] According to them, the dimer spectrum exhibits new absorption peaks around 15.6 and 27.0 kK.

In discussing the experimental results, the crystalline $TCNQ^-$ simple salts can be divided into two classes: those with low electrical conductivity and those with high conductivity.[10] These two classes are not well-defined, but this classification facilitates the presentation of the results and the discussion.

Low-conductivity Compounds. All of the simple salts except the *N*-methylphenazinium salt belong to this group. These compounds have conductivities of 10^{-4} $\Omega^{-1}cm^{-1}$ or less and activation energies as high as 0.3 eV.[9,10] As for the magnetic properties, they are diamagnetic at low temperatures, and at higher temperatures are still diamagnetic or exhibit a small paramagnetic contribution to the susceptibility, which increases with an increase in the temperature. This phenomenon has been tentatively interpreted in terms of a ground singlet and an excited triplet equilibrium

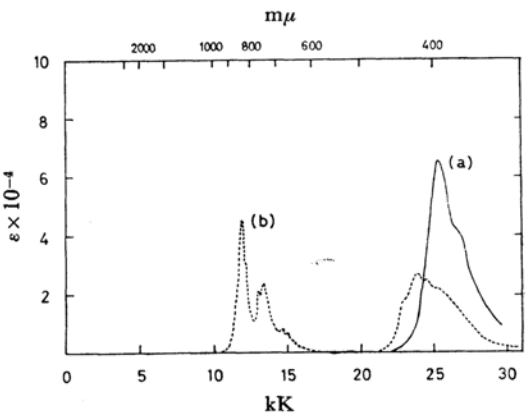

Fig. 1. Absorption spectra of TCNQ (Curve a) and K^+TCNQ^- (Curve b) in acetonitrile solution.

with a relatively high energy separation.[8] If this is the case, the weak paramagnetic contribution is due to the population in the thermally-accessible triplet state. The paramagnetic contribution (χ) to the susceptibility is written as:

$$\chi = \frac{2Ng^2\beta^2}{kT[3 + \exp(J/kT)]} \quad (1)$$

where N is the number of spin-coupled pairs and J, the singlet-triplet energy separation.

In the following paragraphs, the results of experiments on sample low-conductivity compounds will be presented and discussed.

K^+TCNQ^-. According to Anderson and Fritchie,[14] this salt crystallizes in a monoclinic system. The crystal structure consists of columns of $TCNQ^-$ with face-to-face stacking parallel to the *a* axis; the molecular axes normal to the molecular plane nearly coincide with the column axis. It is not clear whether or not there is an alternation in the inter-radical spacings within the column. Unless one assumes such an alternation, the inter-radical spacing is 3.4—3.5 Å.

The absorption spectrum in acetonitrile has already been illustrated in Fig. 1, Curve b. The crystalline spectrum (Fig. 2, Curve a) shows a similarity to that of the $TCNQ^-$ dimer in an aqueous solution.[13] The crystalline spectrum has peaks at 8.5, 16.4, and 27.8 kK. The latter two peaks almost agree with the 15.6 and 27.0 kK peaks respectively in the dimer spectrum. The nature of these bands in the solid state is not clear, but the bands should be assigned to the shifted bands of the $TCNQ^-$ monomer. The low-energy band at 8.5 kK observed in the solid state should correspond to the charge-transfer transition between the anion radicals. If this is the case, its electronic transiton will be allowed with the polarization out

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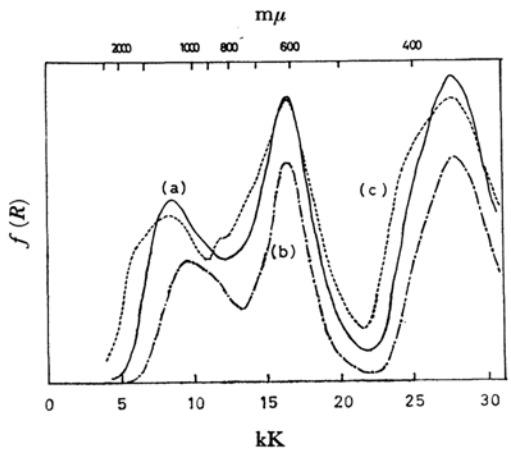

Fig. 2. Crystalline electronic spectra of K^+ $TCNQ^-$ (Curve a), Morpholinium$^+$ $TCNQ^-$ (Curve b) and Li^+ $TCNQ^-$ (Curve c).

of the molecular plane (*i. e.*, along the *a* crystal axis). Anderson and Fritchie have confirmed this prediction experimentally using a near-normal incident reflection.[14] The corresponding charge-transfer band of the dimer in the solution has not yet been obtained, presumably because of the absorption of the solvent. The present question is whether the system of the linear chain column of $TCNQ^-$ with molecular spacing as relatively long, as 3.4—3.5 Å should exhibit a spectral resemblance to the dimer. The electronic state of the isolated ion radical dimer has been examined by Hausser and Murrell.[15] If the spacings are strongly alternate in such a solid, the electronic state might appear to be similar to that in the dimer. However, even if we accept the assumption, the charge-transfer energy in such an ionic crystal should be appreciably different from that in an isolated dimer. Accordingly, the charge-transfer band observed at 8.5 kK is regarded as "crystalline." Nevertheless, because of the experimental similarity of the crystalline spectrum to that of the dimer in the region of high-energy bands, it must be emphasized that all the crystalline electronic state except for the charge-transfer process may be described approximately in terms of the dimer. The approximation might become probable by assuming one of the two possibilities, namely, that ion radicals are equally spaced and weakly coupled with two neighbors each or that ion radicals are alternatingly spaced and rather strongly coupled with one neighbor each. That the molecular spacing, 3.4—3.5 Å, in the case of equally-spaced ion radicals is regarded as relatively long compared with that of a high-conductivity compound (see below) affords evidence for the "weakly-coupled" nature in the former case. The finding that this salt has a low electrical conductivity and a high activation energy[10] supports both possibilities. On the other hand, its almost diamagnetic susceptibility (-1.3×10^{-4} emu/mol at 300°K)[16] has been tentatively described by Eq. (1) with $J\sim0.2$ eV.[8] This description may imply a strong alternation in $TCNQ^-$ stacking, which will support the latter assumption. Under these circumstances, further, detailed study of the crystal structure analysis is necessary to distinguish these two possibilities. At any rate, at the present time, its magnetic property is regarded as based on a non-alternating or alternating linear-chain Heisenberg antiferromagnet, which should produce its almost diamagnetic susceptibility, as is almost the case with certain Würster's salts.[1] Again in TCNQ salts, the contribution of the charge-transfer interaction to the antiferromagnetic interaction is important.

Morpholinium$^+$ $TCNQ^-$. According to Maréchal and McConnell,[17] this substance crystallizes with triclinic symmetry. Its absorption spectrum in acetonitrile is the same as that of the potassium salt. The crystalline spectrum (Fig. 2, Curve b) also exhibits a similarity to that of the dimer. The band peaks are located at 9.5, 16.3, and 27.7 kK. The band at 9.5 kK corresponds to the charge-transfer transition. The latter two bands should be identified as shifted bands of the $TCNQ^-$ monomer.

Here, in this salt, the magnetic property has been well described by Eq. (1) with $J=0.41$ eV.[5] The triplet-state spin-Hamiltonian is written as:

$$\mathcal{H} = \beta \boldsymbol{H}\cdot g\cdot \boldsymbol{S} + DS_z^2 + E(S_x^2 - S_y^2) \qquad (2)$$

where D and E are zero-field splitting parameters. It has been found by ESR study[17] that the z and x axes of the fine-structure Hamiltonian are approximately coincident with the (111) and ($1\bar{1}0$) axes respectively. Here, one assumes a $TCNQ^-$ dimer with a D_{2h} symmetry of face-to-face stacking, where the z and x axes are normal to and along the short axis of the molecules respectively. Theoretical values of D and E can be calculated approximately in terms of magnetic dipole-dipole interaction between unpaired electrons in the dimer. If one uses the spin densities of free $TCNQ^-$ given by Rieger and Fraenkel[18] and the molecular structure given by Hanson,[19] the D and E *versus* inter-planar spacing (z) of the dimer shown in Fig. 3 can be obtained.*2 In order to coincide with the experimental results of $|D|_{obs}=450.2\pm0.4$ and $|E|_{obs}=$

15) K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).

16) R. G. Kepler, P. E. Bierstedt and R. E. Merrifield, *Phys. Rev. Letters*, **5**, 503 (1960).

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*2 The calculations were carried out on the NEAC 2203G in the Computer Center, Hokkaido University.

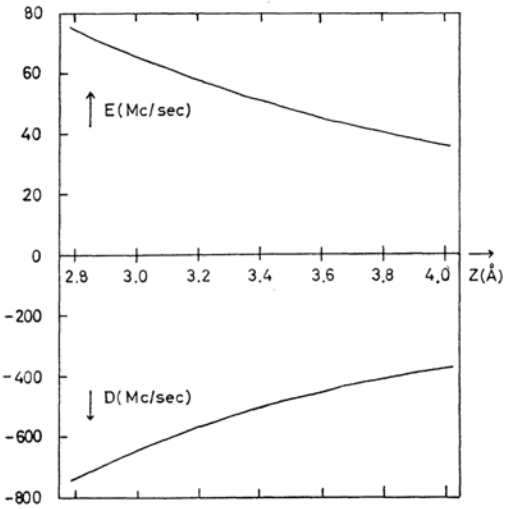

Fig. 3. Calculated zero-field splitting parameters (D and E) in the triplet state of $TCNQ^-$ dimer in Eq. (2) *versus* intermolecular spacing (z).

53.82±0.12 Mc/sec by Marechal and McConnell,[17] z should be 3.4—3.5 Å. Although the crystal structure is not yet available in detail, the estimated value of z is quite reasonable compared to the 3.4—3.5 Å in the potassium salt. Therefore, it may be concluded that $TCNQ^-$ molecules in the morpholinium salt pair up to produce a dimer with an almost D_{2h} symmetry. Its crystalline spectrum supports this conclusion.

Although there exists a rough resemblance of the crystalline spectra and even an exact agreement in high-energy bands between the potassium and the morpholinium salts, their low-energy charge-transfer band peaks show a shift of 1.0 kK; this shift is considered to be due to the difference in the modes of $TCNQ^-$ stacking and/or to that in the sizes of the cations between these two salts. In addition, the finding of a remarkable difference in their electrical conductivities at 23°C between the potassium salt (1×10^{-4} $\Omega^{-1}cm^{-1}$)[10] and the morpholinium salt (1×10^{-9} $\Omega^{-1}cm^{-1}$)[10] may also indicate the importance of the difference in $TCNQ^-$ stacking modes between them.

In connection with the calculations of D and E, it should be mentioned that the lowest triplet wave-function cannot be mixed theoretically with the charge-transfer configuration conceived, because the charge-transfer configuration is a singlet and mixing is forbidden by the spin multiplicity. Thus, the triplet state is probably repulsive.[15] This concept implies that the spin densities in the triplet state of the dimer may be approximately described in terms of the individual doublet spin densities. This speculation is strongly supported by the finding that the observed D and E values in the triplet state are well represented by the magnetic dipole-dipole interaction between a pair of anion radicals with doublet spin densities.

The Other Compounds. All of the other compounds with low conductivity exhibit, more or less, a spectral resemblance to the spectra of the potassium or the morpholinium salt. The three band peaks of their crystalline spectra listed in Table 1 are designated as CT-, α-, and β-bands in the order of increasing energy. Apparently, the locations of the corresponding bands, especially the low-energy charge-transfer (CT) bands, in these compounds depend on the kind of cation. The main reason for the band shifts is also the difference in the modes of $TCNQ^-$ stacking in the crystal and/or that in the sizes of the cations. Nonetheless, all of them have relatively weak interactions among unpaired electrons, producing the rough resemblance of the spectra to that of the dimer.

Table 1. The data for three band peaks in the crystalline electronic spectra of the low-conductivity compounds

Compound	CT-Band (kK)	α-Band (kK)	β-Band (kK)
Li^+TCNQ^-	8.2	16.2	27.5
Na^+TCNQ^-	9.3	16.3	27.5
K^+TCNQ^-	8.5	16.4	27.8
$NH_4^+TCNQ^-$	8.9	16.3	27.8
Triethylammonium$^+$ $TCNQ^-$	8.7	16.4	27.6
Methyltriphenyl-phosphonium$^+TCNQ^-$	10.3	15.3	26.7
Methyltriphenyl-arsonium$^+TCNQ^-$	10.3	15.2	26.3
Morpholinium$^+TCNQ^-$	9.5	16.3	27.7
N-Methylquinolinium$^+$ $TCNQ^-$	9.4	16.1	27.0

In Li^+TCNQ^- the slight but distinct peak at 11.9 kK in the crystalline spectrum (Fig. 2, Curve c) must be noted. It probably arises from the $TCNQ^-$ monomer in some kinds of defects, because in this salt an appreciable ionic conduction, presumably due to the defect, has been found to contribute to its electrical conductivity.[20]

High-conductivity Compound. *N*-Methylphenazinium$^+$ $TCNQ^-$ is the only example exhibiting an electrical conductivity as high as $1.4\times10^2\Omega^{-1}cm^{-1}$. According to Fritchie,[21] it crystallizes as blue-black needles with triclinic symmetry. $TCNQ^-$ molecules form a charge-transfer-bonded, regular, linear chain column parallel to the a crystal axis, with interplanar spacing of 3.26 Å and without any interplanar distance alternation. It is noteworthy that this interplanar spacing is relatively short compared with the 3.4—3.5 Å in the low-conductivity compounds.

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

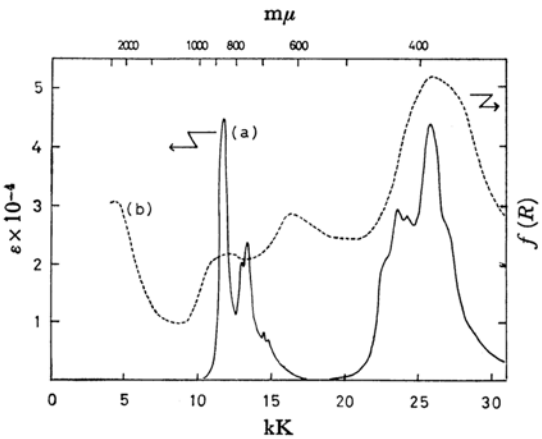

Fig. 4. Absorption spectrum in acetonitrile solution (Curve a) and crystalline electronic spectrum (Curve b) of *N*-Methylphenazinium$^+$ TCNQ$^-$.

The absorption spectrum of the *N*-methylphenazinium salt in acetonitrile, shown in Fig. 4, Curve a, is essentially the same as that of the potassium salt, with the addition of the cation spectrum peak at 25.8 kK. The crystalline spectrum, shown in Fig. 4, Curve b, has peaks at 4.3, 11.8, 16.4, and 25.8 kK. In the previous section the low-conductivity compounds have been found to exhibit approximately the dimer spectrum, whereas the spectrum of the *N*-methylphenazinium salt bears no resemblance to those of the low-conductivity compounds. This must be due to the difference in the manners of TCNQ$^-$ intermolecular interactions in the solid state. It has been demonstrated that some Würster's salts with more-than-pairwise and strong intermolecular interaction exhibit spectra different from either the monomer or dimer spectrum and extending to the lower-energy region.[1] Furthermore, Würster's red bromide has two charge-transfer bands in the low-energy region.[1] Being similar to these salts, the *N*-methylphenazinium salt is characterized by a "strongly-coupled" linear chain system, in which the lowest-energy band observed, at 4.3 kK, may be regarded as an inter-radical charge-transfer absorption. There is a possibility that the band at 11.8 kK is due to the second charge-transfer band or to the shifted band of the TCNQ$^-$ monomer; this point, not yet clear, may be distinguished by means of the polarized spectrum. Although the natures of the bands at 16.4 and 25.8 kK may be similar to those of the α- and β-bands in the low-conductivity compounds respectively, the band at 25.8 kK should comprise that of the cation spectrum, too. However, it must be noted that the elctronic absorption bands in the *N*-methylphenazinium salt are appreciably diffused and continuously overlap with each other. In addition, the facts that the *N*-methylphenazinium salt is the most highly electrically conductive organic compound[11] and that the ions are arranged as a "strongly-coupled" linear chain[21] would imply the delocalization of the unpaired electrons, probably leading to the establishment of a band model for the electrical conduction. It is likely that the lowest-energy band, at 4.3 kK, identified as an inter-radical charge-transfer band, may be associated with the transition from the valence band to the conduction band.[22] Although further work is necessary to explain the relation fully, this speculation is supported by the finding that highly conductive "complex" salts of TCNQ also show a strong low-energy band with an absorption peak around 2—3 kK (see Ref. 23).

Summary

We have divided TCNQ$^-$ simple salts into low- and high-conductivity compounds.

Although the mode of TCNQ$^-$ stacking in the low-conductivity compounds is the dimer (*e. g.*, the morpholinium salt) or the infinite linear chain with equally-spaced ion radicals (*e g.*, one with the assumed model for the potassium salt), the molecular spacings are regarded as being as large as 3.4—3.5 Å in these systems. This gives rise to a relatively small overlap integral of unpaired-electron molecular orbitals between the nearest-neighbor ion radicals. Their crystalline spectra resemble that of the dimer in an aqueous solution, exhibiting the charge-transfer band around 9 kK. Charge-transfer interaction should contribute significantly to the stabilization of antiferromagnetic interaction, resulting in their almost diamagnetic susceptibilities and, in some cases, a singlet-triplet equilibrium for the dimer. The relatively small overlap integral still produces their low electrical conductivities and high activation energies. The relations between the overlap integral and these physical properties remain to be elucidated.

The mode of TCNQ$^-$ stacking in the *N*-methylphenazinium salt is an infinite linear chain column with molecular spacing as little as 3.26 Å. Therefore, the overlap integral of unpaired-electron molecular orbitals is regarded as large. The crystalline spectrum bears no resemblance to those of the low-conductivity compounds and has a low-energy charge-transfer band at 4.3 kK; the reason for this is probably related to its unusually high electrical conductivity.

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