Electrical Conductivity of Single Crystals of *N*-Methylphenazinium–TCNQ and Rb–TCNQ

Genshiro Fujii, Ichimin Shirotani, and Hiroshi Nagano
The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106

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Temperature and pressure dependence of the electrical conductivity of NMP(I)–, NMP(II)–, Rb(I)– and Rb(II)–TCNQ single crystals was studied. NMP(I)–TCNQ showing diffuse streaks was found to have a semiconductive behavior at atmospheric pressure and no conductive maximum appeared at low temperatures. Moreover the metallic behavior was not shown even at 100 kbar. The crystal structure of NMP(II)–TCNQ is not similar to that of NMP(I)–TCNQ. The difference of physical properties of two phases is discussed. The anomalous electrical behavior in the pressure range from 1 bar to 40 kbar was observed for Rb(I)–TCNQ. The resistivity of Rb(II)–TCNQ decreased monotonously with increasing pressure. The magnitude of their activation energies was 0.15 eV for Rb(I) salt and 0.11 eV for Rb(II) salt at 100 kbar. The insulator to metal transition could not be observed at least up to 100 kbar.

Physical properties of TCNQ (tetracyanoquinodimethane) salts which are quasi one-dimensional conductors have been a subject of considerable interest in recent years. NMP (*N*-Methylphenazininum)–TCNQ and Rb–TCNQ are polymorphic having two crystalline forms at room temperature. One is a triclinic phase (NMP(I)–TCNQ, Rb(II)–TCNQ) and the other is a monoclinic phase (NMP(II)–TCNQ, Rb(I)–TCNQ).

The crystal structure of NMP(I)–TCNQ consists of linear chains of TCNQ$^-$ anions and parallel chains of NMP$^+$ cations.1,2) The crystals of this phase are one of the most highly conductive ion-radical salts. The electrical,3–5) magnetic,6) and optical7,8) properties have been intensively studied. The conduction mechanism in NMP(I)–TCNQ crystal has been particularly discussed by many authors.

The monoclinic phase of NMP(II)–TCNQ shows semiconductive behavior; $\rho \approx 10^4\ \Omega$ cm at room temperature with an activation energy of 0.4 eV.9) NMP$^+$ cations and TCNQ$^-$ anions alternate in columns parallel to the c axis.10) The columnar structure of NMP(II)–TCNQ is remarkably different from that of NMP(I)–TCNQ.

Rb(I)–TCNQ has monoclinic symmetry and the TCNQ$^-$ anions are stacked face to face to form columns of diadic units of a TCNQ$^-$. Within a column, two different intermolecular spacings, 3.159 and 3.484 Å, appear alternately.11)

The X-ray study of Rb(II)–TCNQ shows a triclinic structure consisting of linear chains of identical TCNQ molecules stacked face to face and equally separated from one another.12) This columnar structure is very similar to that found in the crystal of NMP(I)–TCNQ. However, the electronic structure of Rb(II)–TCNQ is remarkably different from that of NMP(I)–TCNQ. The differences of the physical properties in both Rb–TCNQ have already been discussed in previous papers.13–15)

In this paper, we present some findings on the temperature and pressure dependence of electrical conductivity in single crystals of NMP– and Rb–TCNQ and discuss the conduction mechanism for these salts.

Experimental

Preparation of Single Crystals. The acetonitrile solvent (Donin Yaku Kagaku, Spectro Grade) was refluxed over P_2O_5 and fractionally distilled. TCNQ (Tokyo Kasei Company) was recrystallized twice from pure acetonitrile and sublimed three times at 120 °C and 10^{-5} Torr. Only brilliant yellow orange TCNQ crystals from the center zone were collected for usage. NMP–TCNQ was prepared by treatment of *N*-methylphenazinium methyl sulfate in hot alcohol with a boiling solution of Li–TCNQ in ethanol.16) Li–TCNQ was prepared by the reaction of TCNQ and anhydrous LiI provided by Hashimoto.17) The phenazine provided by Anzai was purified by zone refining and sublimation.

Black needle single crystals of NMP(I)–TCNQ were grown from saturated acetonitrile solutions by fast recrystallization. The largest crystal obtained was $0.6\times0.08\times5$ mm^3. Single crystals prepared by us showed the diffuse streaks along the c* direction.2) Crystals of NMP(II)–TCNQ were grown from dilute acetonitrile solutions by very slow recrystallization.

The preparation of Rb–TCNQ has been reported in detail previously.13)

Electrical Measurements. DC four-probe resistance measurements were made on single crystals of NMP–TCNQ and Rb–TCNQ along the needle axis parallel to the TCNQ stacks. The gold wires (0.02 mm diameter) were used for electrical lead wires. Electrical contact with the crystals was made by wetting the electrical lead wires with a silver paste paint. Using this arrangement, the crystals could be thermally cycled without damage. The sample holder, in which the sample was already placed, was mounted in a vacuum can of a temperature-variable cryostat. The temperature, which was controlled by helium exchange gas and a heater, was determined by means of a copper-constantan thermocouple.

Measurements of electrical resistance as a function of pressure were made using a clamped-type high-pressure anvils-apparatus as previously described.18)

Optical measurements have been made by the same manner as described previously.13)

Results and Discussion

NMP(I)–TCNQ. Fritchie's average structure of NMP(I)–TCNQ shows that NMP$^+$ cation is located at the position (1/2, 1/2, 1/2) in unit cell,taking either of the two possible orientations of the methyl groups as equally probable1). On the basis of this structure, Bloch *et al.*5) have tried to apply the theory of hopping in disordered systems to the conductivity of NMP(I)–TCNQ. The hopping theory for one dimensional disordered system predicts $\ln\sigma(T)=\ln\sigma_0-(T_0/T).^{1/2}$ They have found that the temperature dependence of the conductivity could be approximately fitted by $\ln\sigma\approx$

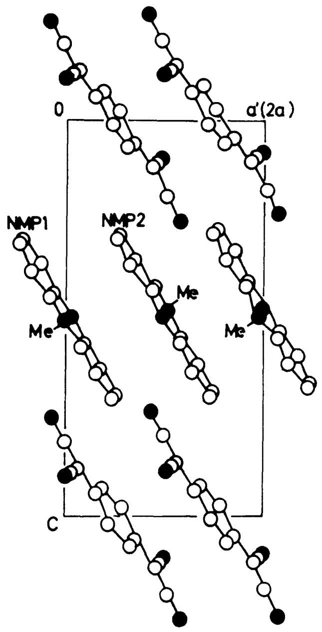


Fig. 1 (a). Crystal structure of NMP(I)–TCNQ showing diffuse streaks along b axis.[2)]

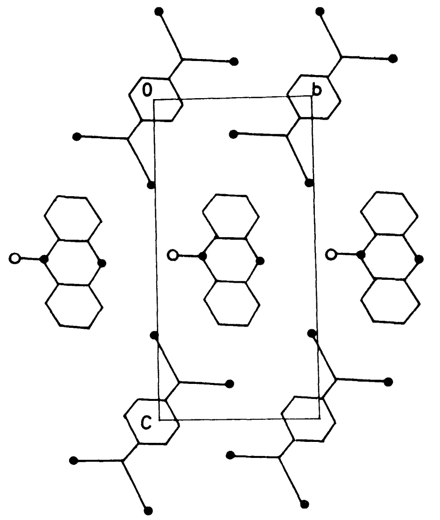


Fig. 1 (b). Crystal structure of NMP(I)–TCNQ showing diffuse streaks along a axis.[2)]

$(T_0/T)^{1/2}$. On the other hand, Coleman *et al.*[4)] have emphasized that the electronic and magnetic properties can be quantitatively described in terms of the one-dimensional Mott-Hubbard model. The temperature dependence of the conductivity of high purity single crystals has revealed that the plot of $\ln(\sigma/\sigma_0)$ *vs.* $1/T$ shows straight-line; this is not consistent with the analysis of Bloch *et al.*

Recently, Kobayashi[2)] has studied an X-ray analysis of high purity single crystal of NMP(I)–TCNQ prepared by us. The X-ray diffraction patterns of this crystal show diffuse streaks along the c* direction. The analysis of the intensities of these streaks reveals that the orientation of NMP$^+$ cation is one-dimensionally disordered along the c axis as is shown in Fig. 1. The structure obtained indicates that the potential exerted on an electron moving in a column of TCNQ is not random, but can be expressed by a periodic function.

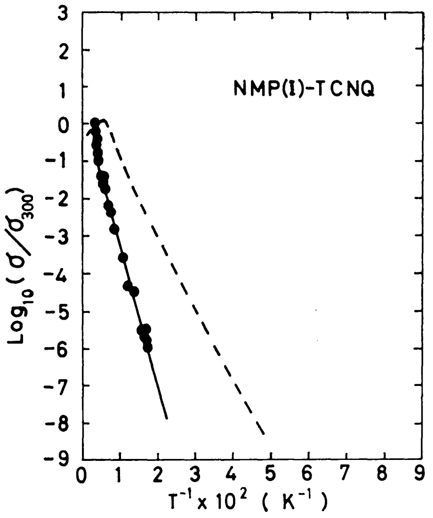
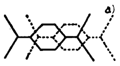
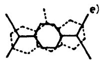
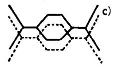
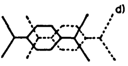


Fig. 2. Temperature dependence of the electrical conductivity for NMP(I)–TCNQ.
●: Present work, ----: Ref. 4.

Table 1. Physical properties of NMP- and Rb-TCNQ.

	NMP — TCNQ		Rb — TCNQ	
Polymorphic form	I	II	I	II
Crystal symmetry	triclinic[a)]	monoclinic[b)]	monoclinic[c)]	triclinic[d)]
Space group	$P\bar{1}$[a)]	$P2_1/n$[b)]	$P2_1/c$[c)]	$P\bar{1}$[d)]
Unit of TCNQ	monadic[a)]		diadic[c)]	monadic[d)]
Interplanarspcing between TCNQ(Å)	3.26[a)]		3.159[c)] 3.484[c)]	3.43[d)]
Model of overlap between nearest molecule	 a)	 e)	 c)	 d)
Resistivity at 1 bar (Ω-cm)	7.7×10^{-3} h) 2.63×10^{-3} f)	1.3×10^4 g)	3×10^5 g)	1×10^2 g)
Activation energy at 1 bar (eV)	0.06 h) 0.037 f)	0.405 b)	0.44 ~ 0.53 g)	0.16 ~ 0.22 g)
Resistivity at 100 kbar (Ω-cm)	1.38×10^{-4} h)	5.75×10^2 h)	7.5×10^2 h)	1.5×10^{-2} h)
Activation energy at 100 kbar (eV)	0.02 h)	0.07 h)	0.15 h)	0.11 h)

a) Ref. 1. b) Ref. 9. c) Ref. 11. d) Ref. 12. e) Ref. 10. f) Ref. 4. g) Ref. 13. h) Present work.

The temperature and pressure dependence of the conductivity of single crystals of NMP(I)–TCNQ showing the diffuse streaks were studied. The conductivity data are presented in Fig. 2, where $\log(\sigma/\sigma_{300})$ is plotted as a function of T^{-1}. The room temperature conductivity was 130 Ω^{-1} cm^{-1}. The activation energy was 0.06 eV as shown in Table 1. No conductivity maximum appeared. This behavior is not consistent with the data reported by Coleman *et al.*[4)]

Morosin[19)] has pointed out that the single crystals supplied by Heeger did not show diffuse streaks. The conductivity of those crystals indicates a metallic state above 200 K with a continuous transition to an insulator below 200 K.[3,4)] Morosin has conjectured that Kobayashi's observation on NMP(I)–TCNQ arose from the disordered regions formed between the twin boundaries of two different phases of NMP–TCNQ. If single crystals are grown from saturated acetonitrile solution by fast recrystallization, crystals of the triclinic phase (NMP(I)–TCNQ) are only found. Crystals prepared by us showed diffuse streaks. Therefore, Kobayashi's observation does not arise from the twin

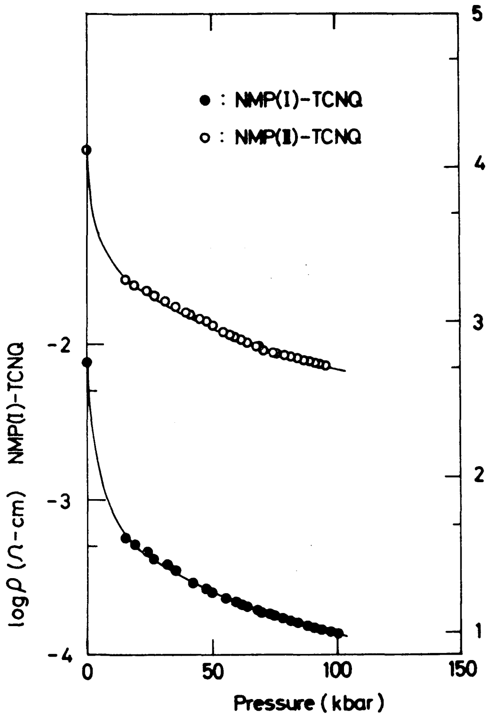


Fig. 3. Pressure dependence of the electrical resistivity for NMP–TCNQ.
●: NMP(I)–TCNQ, ○: NMP(II)–TCNQ.

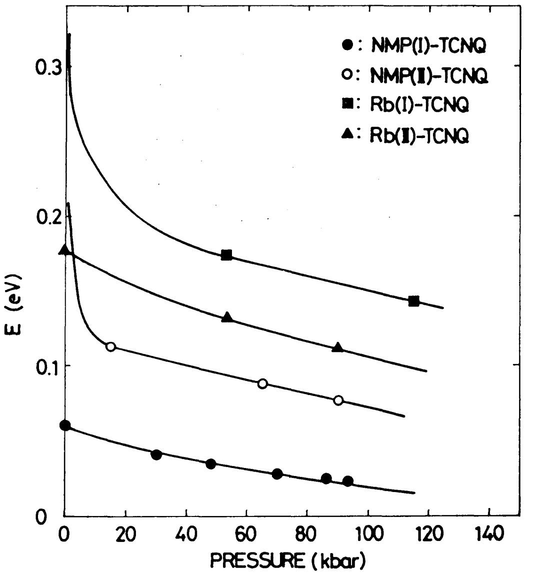


Fig. 4. Pressure dependence of activation energy for NMP– and Rb–TCNQ.
●: NMP(I)–TCNQ, ○: NMP(II)–TCNQ, ■: Rb(I)–TCNQ, ▲: Rb(II)–TCNQ.

boundaries of two phases, but is the intrinsic property of NMP(I)–TCNQ. There is an apparent difference in the columnar structure of NMP$^+$ between Heeger's crystals and ours. This inconsistency may be due to the difference of the method of sample preparation.

As is shown in Fig. 1, the positive potential exerting on an electron moving in a column of TCNQ can be expressed by the periodic function. Therefore, the corresponding energy band has not to be a half-filled band, but a filled band.[2] It seems to be reasonable that the electrical behavior in NMP(I)–TCNQ showing diffuse streaks is semiconductive.

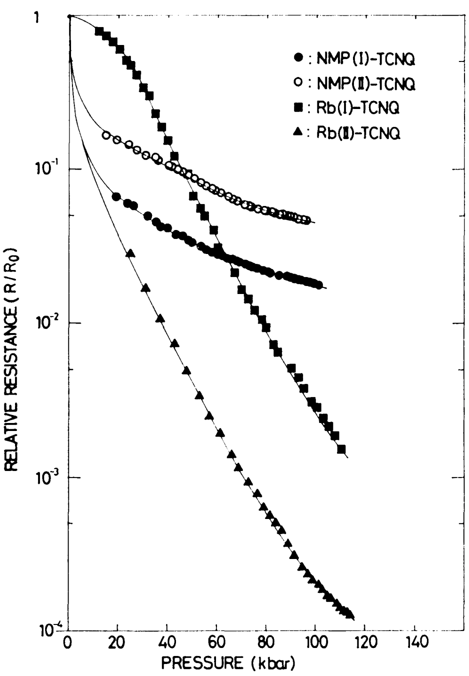


Fig. 5. Pressure dependence of relative resistance for NMP– and Rb–TCNQ.
●: NMP(I)–TCNQ, ○: NMP(II)–TCNQ, ■: Rb(I)–TCNQ, ▲: Rb(II)–TCNQ.

The pressure effect on electrical resistivity of this single crystals was measured along the conductive axis up to 100 kbar at room temperature. The result is shown in Fig. 3. The electrical resistivity decreased with increasing pressure. The resistivity at 100 kbar was 1.38×10^{-4} Ωcm. Figure 4 exhibits the pressure dependence of the activation energies of the TCNQ salts. The activation energy of NMP(I)–TCNQ rapidly decreased up to 20 kbar. It was 0.02 eV at 100 kbar. NMP(I)–TCNQ showing diffuse streaks did not show the metallic behavior even at 100 kbar.

NMP(II)–TCNQ. This compound crystallizes in space group $P2_1/n$ with $a=10.558$, $b=25.952$, $c=7.0872$ Å, $\alpha=90.68°$, and $z=4$.[10] The anion and cation alternate in the column parallel to the c axis with slightly unequal interplanar spacings. This structure does not resemble that of NMP(I)–TCNQ. Coleman *et al.*[9] have already studied the temperature dependence of the electrical conductivity for NMP(II)–TCNQ; this monoclinic phase is semiconductive with a room temperature conductivity of 7.67×10^{-5} Ω^{-1} cm^{-1} and an energy gap of 0.81 ± 0.02 eV.

Recently the absorption spectra of two crystalline forms have been studied by Tanaka *et al.*[8] Their absorption spectra are very different. The lowest energy transition in NMP(I)–TCNQ appears along the a axis at 5500 cm^{-1}. This band is assigned to an intermolecular transition between TCNQ molecules. On the other hand, the CT band in NMP(II)–TCNQ is observed at near 8000 cm^{-1}. This band corresponds to a charge transfer of an electron from the NMP molecule to TCNQ. The large difference between electrical and optical properties of such two-phase salts indicates a crucial role of crystal structure of an organic salt. Mulliken[20)] discussed the effect of pressure on electronic state of D^+A^- complexes and predicted a red shift and an increase of absorption intensity of a CT band and a decreased resistivity with increasing pressure. The majority of D^+A^- complexes show a decrease in resistivity with increasing pressure.[21,22)] As shown in Figs. 3 and 4 the electrical resistivity and the activation energy in NMP(II)–TCNQ single crystals rapidly droped in the low pressure region and above 30 kbar decreased monotonously with increasing pressure. Figure 5 exhibits the ratio of the resistance, $\log R/R_0$, for both NMP–TCNQ. Above 30 kbar the rate of the pressure change of resistivity for the NMP(I) salt is approximately equal to that for the NMP(II) salt.

The values of their activation energies ($\Delta E_{\rm I}$ and $\Delta E_{\rm II}$) decrease in the rate of

$$(\partial\Delta E_{\rm I}/\partial P)_T = -3.5\times10^{-4}\ \text{eV/kbar}$$

$$(\partial\Delta E_{\rm II}/\partial P)_T = -4.4\times10^{-4}\ \text{eV/kbar}.$$

These values are nearly equal, though the crystal structures of both NMP–TCNQ are significantly different. This may have arisen from the comparable compressibility between the two phases. Similar electrical behavior was found for both Rb–TCNQ salts, as discussed in the next section.

We suggest that the electrical behavior of these salts above 30 kbar may mainly be due to the increase of interchain interactions.

Rb(I)- and Rb(II)-TCNQ. Phase transitions and electrical and optical properties in both Rb salts have been already studied.[13)] The relation between those properties and crystal structures have been discussed in the previous paper.[14)] The electrical resistance of powdered Rb–TCNQ has been measured up to 500 kbar at room temperature.[15)] The lowest resistivity for the Rb(I) salt is 1 Ωcm at 135 kbar, while that for the Rb(II) salt is 0.06 Ωcm at 170 kbar.

Figure 6 shows the effect of pressure on the resistance of single crystals of Rb(I)- and Rb(II)-TCNQ. The positive slope of the electrical resistance in the pressure range from 1 bar to 40 kbar was observed for the Rb(I) salt. Since the pressure induced phase transition in Rb(I)–TCNQ has been found at about 3.5 kbar,[13)] this positive slope may be due to the appearance of a high pressure phase at quasi hydrostatic pressure. The activation energy was 0.15 eV at 100 kbar. A phase transition to a metallic state was not observed.

The resistivity of Rb(II)–TCNQ decreased monotonically with increasing pressure. The resistivity along the conductive axis was 1.5×10^{-2} Ωcm and the activation energy was 0.11 eV at 100 kbar. The compressibility of Rb(II)–TCNQ has not been measured, but it is probably comparable to that of aromatic crystals. From the relation between the pressure and the volume for molecular solid given by Samara and Drickamer,[23)] the average intermolecular distance at 100 kbar was estimated to be about 90% of that at atmospheric pressure. Therefore, we can estimate the interplanar spacings between TCNQ molecules in the Rb(II) salt around at 100 kbar to be shorter than that in metallic TCNQ salts at 1 bar.[21)] However, metallic behavior could not be observed in Rb(II)–TCNQ at 100 kbar

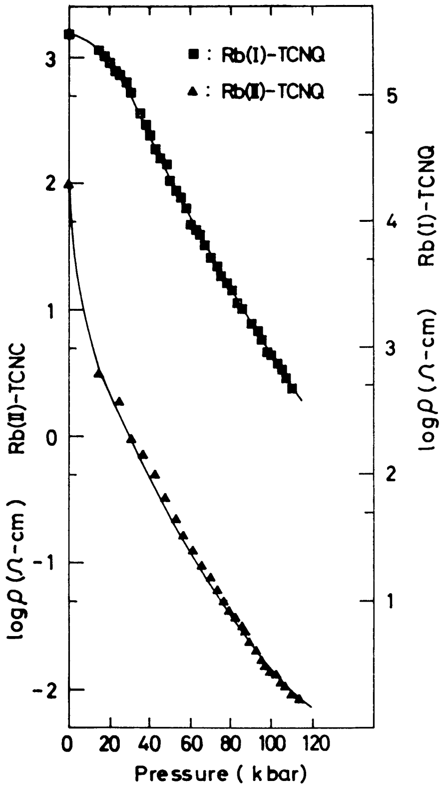


Fig. 6. Pressure dependence of electrical resistivity for Rb–TCNQ.
■: Rb(I)–TCNQ, ▲: Rb(II)–TCNQ.

The large difference in the conductivity of Rb(II)- and NMP(I)–TCNQ at atmospheric pressure has been mainly explained by two models. LeBlanc[25)] suggested that the excitonic polarizability of the cation is the more important determinant of the variation in conductivities. On the other hand, Torrance *et al.*[7)] proposed the new model in which the large conductivity of NMP(I)–TCNQ is attributed to incomplete charge transfer from the aromatic cation to TCNQ.

Figure 7 shows the effect of pressure on the absorption spectra of NMP(I)–TCNQ at room temperature. The absorption spectrum of NMP(I)–TCNQ is similar to that of complex salts such as Q– and Ad–TCNQ$_2$. The absorption bands have been assigned by Torrance *et al.*[7)] and Tanaka *et al.*[8)]

The pressure induced absorption band observed at around 20×10^3 cm^{-1} for NMP(I)–TCNQ has also been found many complex salts.[26)] Oohashi and Sakata[27)] have suggested that the new band at high pressure may be assigned to the $8\rightarrow9'$ CT transition from TCNQ$^-$ to TCNQ^0. This shows that there may be neutral TCNQ molecules in NMP(I)–TCNQ. The incomplete charge transfer from NMP to TCNQ has been discussed by Butler *et al.*[28)] and Kwak *et al.*[29)] Ukei[30)] has observed new weak X-ray diffuse streaks in addition to Kobayashi's observation. These diffuse lines can be interpreted in terms of a Kohn anomaly. From the observed superperiod the degree of charge transfer is estimated. The characteristic electrical and optical behavior in NMP(I)–TCNQ arises from the incomplete charge transfer from NMP to TCNQ.

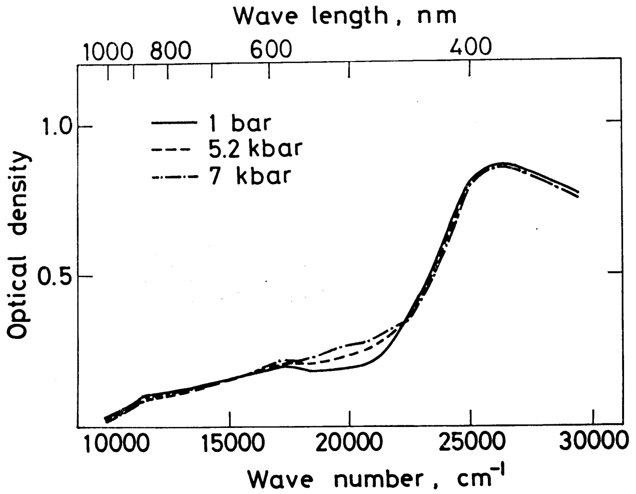


Fig. 7. Effect of pressure on the absorption spectra for NMP(I)-TCNQ.
——: 1 bar, ----: 5.2 kbar, —·—: 7 kbar.

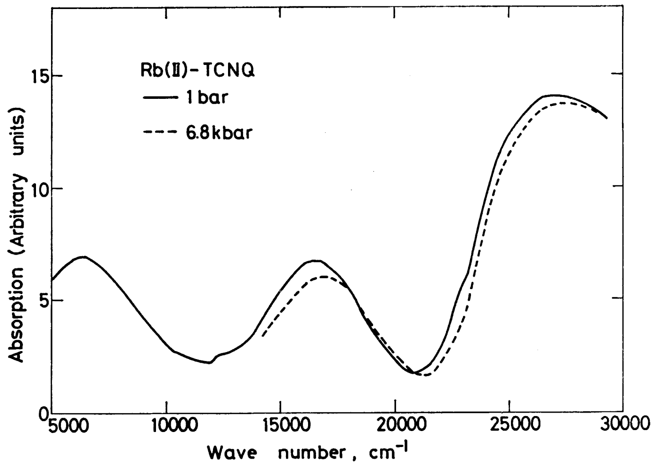


Fig. 8. Pressure effect on absorption spectra for Rb(II)-TCNQ.
——: 1 bar, ----: 6.8 kbar.

Figure 8 illustrates the pressure effect on absorption spectra of Rb(II)-TCNQ at room temperature. The absorption bands in the visible region are the locally excited (LE) bands within the TCNQ$^-$ anion. These exhibit the spectral blue shift with increasing pressure. The rate of pressure shift was +67 cm^{-1}/kbar for 26.2 $\times 10^3$cm^{-1} band and +62 cm^{-1}/kbar for 16.1 $\times 10^3$ cm^{-1} band. The near-infrared band at around 5.5 $\times 10^3$ cm^{-1} is assigned to the charge transfer band between TCNQ$^-$ anions. The pressure effect on the CT band could not be observed because of interference by the pressure-transmitting fluid. The absorption spectrum of Rb(II)-TCNQ is markedly different from that of NMP(I)-TCNQ.

Rb(II)-TCNQ is fully charge transferred from Rb to TCNQ. Torrance *et al.*[8] have pointed out that in the case of complete charge transfer the lower Hubbard band was full; such a compound was a Mott insulator. Though NMP- and Rb-TCNQ are 1 : 1 simple salts, their electronic structures are essentially different. The conductivity along the conductive axis for the Rb(II) salt at 100 kbar is smaller than that of the NMP(I) salt at 1 bar, and the Rb(II) salt does not indicate the metallic behavior at 100 kbar though we can expect the interplanar distance between TCNQ molecules in the Rb(II) salt at 100 kbar to be shorter than 3.26 Å in NMP(I)-TCNQ at 1 bar. These results indicate that the electrical conductivity depends not only on the molecular distance between TCNQ molecule but also to a good extent on the electronic structure of TCNQ salts.

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