BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (9), 2358—2373 (1976)

Electronic Spectra and Electronic Structure of TCNQ Complexes

Jiro TANAKA, Masashi TANAKA, Takashi KAWAI, Teruhiro TAKABE, and Osamu MAKI
Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464

(Received December 11, 1975)

Electronic spectra of several TCNQ complexes have been measured with single crystals by the transmission method. The assignment of electronic transitions are presented based on the electronic structure of the crystals. The molecular viewpoint is stressed in a theoretical treatment. The spectra are interpreted in terms of the charge transfer between TCNQ species and the local transitions of TCNQ and the donor molecules. It is shown that the electronic structure of the crystal may be deduced from the spectral analysis. The magnetic and electric properties of several conducting TCNQ complexes are discussed by this model with the wavefunctions determined by a theoretical calculation and the analysis of the spectral results.

Electronic absorption spectra of TCNQ complexes have been investigated for single crystals and powdered samples by many people. Although there have been many comprehensive papers and reviews on the structural, electronic and magnetic properties of these crystals,[1–5] but the interesting electronic processes of these complexes are still not satisfactorily explained in a comprehensive way.

Recently the study on optical spectra becomes more important, because the remarkable electronic properties of high conductive TCNQ salts may be elucidated by the analysis of their electronic spectra. In the present paper we will discuss the single crystal electronic absorption spectra of several TCNQ complexes, together with the discussions of the electronic structures and the intermolecular interactions. The interpretation of the electronic spectra is presented and the magnetic and electric properties are studied with the model calculation. The aim of this paper is to give an unified view on different aspects of physical properties based on the chemical constitution and electronic structure of the crystals. We try to find a reasonable concept of the characteristic properties of organic conductors from structural points of view, hoping that this analysis will be a useful guide for the design and synthesis of new conducting organic materials. It will be shown that the electronic spectrum may give a useful diagonosis on the electronic structure of TCNQ complexes.

Experimental

The materials were prepared by the methods of Melby *et al.*[6] and Melby.[7] Very thin crystals were prepared by recrystallization from dry acetonitrile and their absorption spectra were measured by the microspectrophotometer designed in this laboratory. The thickness of the crystals used for the transmission measurement was less than a few micron, but it was difficult to measure the thickness very accurately.

The spectrophotometer consists of a light source, a monochromator of Carl Zeiss M4Q and a detector with a PbS photocell and a HTV 446 photomultiplier tube. An Olympus microscope was used with Carl Zeiss Ultrafluar objectives of 32 and 100 magnifing power. The lenses are achromatic for 700—230 nm, but it is not guaranteed for the near infrared region, therefore we have used possibly large crystals to avoid the effect of aberration. A quartz polarizer of Rochon type was used to obtain a polarized light. The crystalline axis and the indices of the developed planes were checked and confirmed by taking X-ray photographs with crystals which were large enough for the X-ray experiment. Sometimes very thin crystals were prepared by recrystallization on a quartz slide glass, and the crystalline habit was checked by the polarizing microscope and compared with the large one determined by the X-ray method.

Crystalline Structure and Electronic Configuration of TCNQ Complexes

The crystals of TCNQ complexes can be classified into two groups, in one group the donor and TCNQ make a stacking pair (D^+A^-), while in the other group TCNQ makes the column by itself ($A\cdot A\cdot A\cdot\cdots$) and the donor forms their own column or take their own positions.[3] In this study we concentrate on the latter type of crystals which is more interesting than the ordinary DA complex. The complexes forming TCNQ columns show variable ratio of the donor to TCNQ; there is a variety of type of (D: A) ratio as 1: 1, 1: 2, 2:3, and 2:4. For complexes having TCNQ more than 1: 1 mole ratio, neutral TCNQ molecules are involved. The names and abbreviations of typical donors or cations are shown in Fig. 1.

The X-ray crystal structure analysis on these complexes revealed that there are a little but significant difference of the bond length between the neutral, negative and a half-ionized TCNQ species. Actually the crystallographic results show that these differently

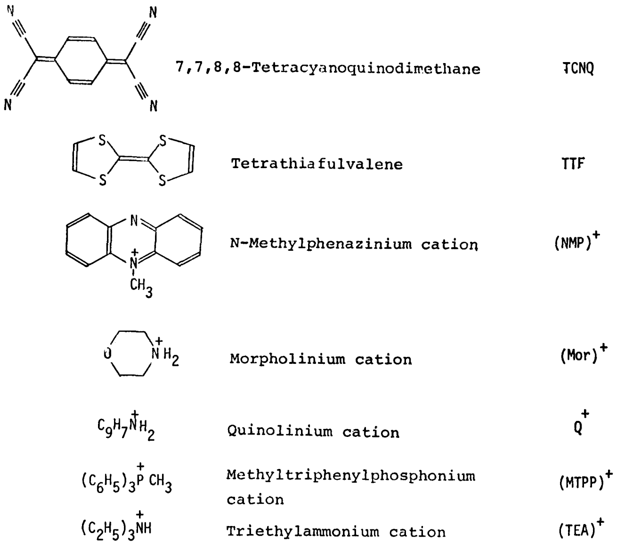


Fig. 1. TCNQ and several donor molecules.

harged species are situated on different sites in the crystal.

In crystals such as Q(TCNQ)$_2$,8)TMPD(TCNQ)$_2$,9) and Ac(TCNQ)$_2$10) the structure of all TCNQ is equivalent, which may imply that the negative charges may be completely delocalized all over the TCNQ columns. However, from a view of strong electron correlation effect between electrons on the same and the nearest neighbour molecules, it seems more reasonable that extra electrons may reside in alternate site to relieve the repulsion. In this case both the negative and the neutral TCNQ coexist, however, it was difficult to discern which is the anion or the neutral species, and the X-ray scattering method will give only an average structure of the charged and neutral molecules. Therefore a most plausible electron configuration of the 1 : 2 type crystal is that the excess electrons are localized on alternate TCNQ site and the neutral TCNQ is sandwiched between anions, and such a locally ordered structure may fluctuate, and a superposition of two alternative structures will give an apparently equivalent crystal structure. We may call this type of electron configuration as an alternant type.

An apparent chemical constitution of the complex does not necessarily mean an equivalence of the electronic structure, for instance, recent X-ray analyses of TTF–TCNQ11–13) show that the bond lengths for TCNQ in this complex are close to a half-charged anion. This is in harmony with recent experiments on ESCA and IR studies of TTF–TCNQ.14,15) These studies give evidences of incomplete charge transfer from TTF to TCNQ that the crystal is considered to contain both $(TCNQ)^0$ and $(TCNQ)^-$. For this reason, it may be more plausible that this crystal has an alternant type structure as its basic configuration rather than that all TTF and TCNQ are singly ionized. Further consideration will be given in later sections.

In crystals with 2: 4 or 2: 3 donor to TCNQ ratio, electrons are thought to be localized on particular paired sites, hence, we may call this type of configuration as an island type.16,17)

In crystal in which all TCNQ have a negative charge, the TCNQ column forms either a linear chain or a dimeric pair, and the phase transition was observed to change the linear form to the dimeric form at low temperature.18,19)

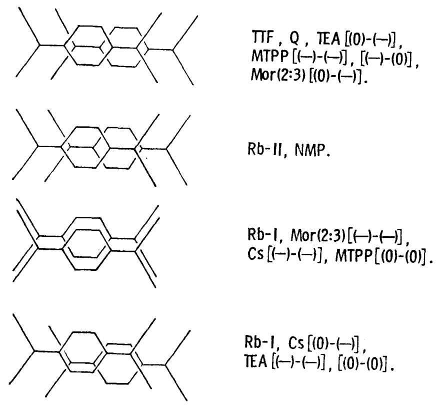


Fig. 3. Nearest neighbour overlap of TCNQ molecules.

In Fig. 2 different types of electron configuration of TCNQ column are schematically classified. The most important type from a view of good electric conduction may be an alternant type and an island type. In the following we will discuss the electron interaction between TCNQ molecules in the crystal by these basic electron configurations. The types of the interactions are the dimer type, the island type and the alternant type. For the linear chain structure, the interaction must be considered to obey the crystal symmetry of the one-dimensional lattice, however, the TCNQ complex we have treated in this paper has a dimeric structure rather than a linear chain structure, therefore our theoretical treatment may be limited to the coupled molecular model. The extension to include the exciton interaction between different cells may not be difficult, but the excited state of CT character may be easily trapped because of their large polarization effect, and empirically the magnitude of the exciton type interaction will be not so significant for such CT complexes, therefore the exciton treatment is not developed in this study.

The mode of overlapping of TCNQ molecules is shown in Fig. 3, and a tendency may be seen that a pair made of neutral and charged TCNQ takes a similar conformation, in which a direct overlap is avoided by displacing one molecule to the other.3) A pair made of both charged TCNQ species takes several different conformations, but it shows a tendency of larger overlap than the former type.

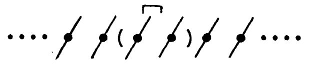
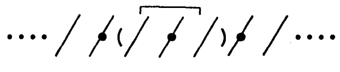
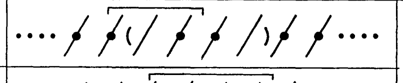
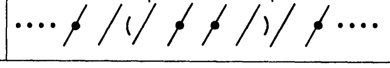
Donors	Ratios of Donor to Acceptor	Electron Configurations	Types of Interactions
Rb,K,Li,Mor	1:1		Dimer Type
TTF,NMP	1:1		Alternant Type
Q,Ac,TMPD	1:2		
Cs,Mor	2:3		Island Type
TEA,MTPP	2:4		

Fig. 2. Electronic configurations of TCNQ columns and types of interactions.

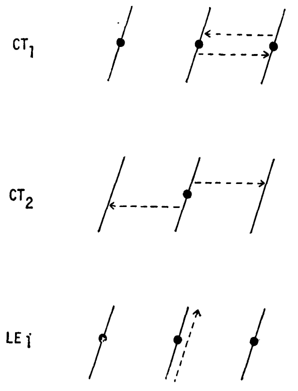


Fig. 4. Basic excited configurations in TCNQ columns.

Theoretical Analysis of Electronic Spectra

The electronic spectra of TCNQ anion in solution was studied by Boyd and Phillips[20] and the molecular orbital calculation was carried out by Lowitz.[21] For the TCNQ complex crystals, Iida[22] has pointed out that there are three types of transitions in the visible and near infrared region. The basic excited configurations are shown in Fig. 4. The LE excited level means locally excited level of TCNQ anion and we denote the lowest one of this kind as LE_1 and the second one by LE_2, and so on. The CT_1 level is the charge transfer between the TCNQ anions and the CT_2 level is the charge transfer from the anion to the neutral TCNQ. In actual crystals, these levels interact to each other, and complicated spectral patterns are observed. In the following we attempt to analyse the spectral features of the complex by calculating the intermolecular interaction between the levels of different TCNQ molecules with the modified Hubbard Hamiltonian,[23,1] which is further modified by our own recipe.

The wavefunction of the system may be described by an antisymmetrized product of the molecular orbitals of the constituent TCNQs. The Hamiltonian of the system may be given by

$$H=\sum_{\mathrm{p}i}\sum_{\mathrm{q}j}\sum_{\sigma}\langle\phi_{\mathrm{p}i}|-\frac{\hbar^2}{2m}\Delta_\mu+\sum_{\mathrm{s}a}V(R_{\mathrm{s}a}-r_\mu)|\phi_{\mathrm{q}j}\rangle a^+_{\mathrm{p}i\sigma}a_{\mathrm{q}j\sigma}$$
$$+\frac{1}{2}\sum_{\mathrm{p}i}\sum_{\mathrm{q}j}\sum_{\mathrm{r}k}\sum_{\mathrm{s}l}\sum_{\sigma\sigma'}(\phi_{\mathrm{p}i}\phi_{\mathrm{s}l}|\phi_{\mathrm{q}j}\phi_{\mathrm{r}k})a^+_{\mathrm{p}i\sigma}a^+_{\mathrm{q}j\sigma'}a_{\mathrm{r}k\sigma'}a_{\mathrm{s}l\sigma} \quad (1)$$

where $\phi_{\mathrm{p}i}$ and $\phi_{\mathrm{q}j}$ denote the i-th and the j-th molecular orbitals of the p and q molecules and σ indicates spin functions. The Coulomb repulsion integral is written with a notation that

$$(\phi_{\mathrm{p}i}\phi_{\mathrm{s}l}|\phi_{\mathrm{q}j}\phi_{\mathrm{r}k})=\int\phi^*_{\mathrm{p}i}(\mu)\phi_{\mathrm{s}l}(\mu)\frac{e^2}{r_{\mu\nu}}\phi^*_{\mathrm{q}j}(\nu)\phi_{\mathrm{r}k}(\nu)\mathrm{d}v_\mu\mathrm{d}v_\nu. \quad (2)$$

In this calculation we restrict our attention to the higher MO of TCNQ, m and m-1, where the singly occupied highest MO in TCNQ$^-$ is written by m and the doubly occupied second highest MO by m-1.

The intermolecular interaction between p and q molecules is considered only for the nearest neighbours, and we retain the interactions which are first order to the electron overlap. Then the Hamiltonian is given by

$$H=\sum_{\mathrm{p.q}}\sum_{i.j=m-1}^{m}\sum_{\sigma}t^{\mathrm{pq}}_{ij}a^+_{\mathrm{p}i\sigma}a_{\mathrm{q}j\sigma}$$
$$+\sum_{\mathrm{p}}U^{\mathrm{pp}}_{mm}n_{\mathrm{p}m\alpha}n_{\mathrm{p}m\beta}+\sum_{\mathrm{p.q}}\sum_{\sigma\sigma'}U^{\mathrm{pq}}_{mm}n_{\mathrm{p}m\sigma}n_{\mathrm{q}m\sigma'}$$
$$+\sum_{\mathrm{p.q}}\sum_{\sigma\sigma'}D_{\mathrm{pq}}a^+_{\mathrm{p}m\sigma}a^+_{\mathrm{q}m-1\sigma'}a_{\mathrm{q}m\sigma'}a_{\mathrm{q}m\sigma} \quad (3)$$

where $$t^{\mathrm{pq}}_{ij}=\langle\phi_{\mathrm{p}i}|-\frac{\hbar^2}{2m}\Delta_\mu+\sum_{\mathrm{s}a}V(R_{\mathrm{s}a}-r)|\phi_{\mathrm{q}j}\rangle \quad (4)$$

$$U^{\mathrm{pp}}_{mm}=(\phi_{\mathrm{p}m}\phi_{\mathrm{p}m}|\phi_{\mathrm{p}m}\phi_{\mathrm{p}m}) \quad (5)$$

$$U^{\mathrm{pq}}_{mm}=(\phi_{\mathrm{p}m}\phi_{\mathrm{p}m}|\phi_{\mathrm{q}m}\phi_{\mathrm{q}m}) \quad (6)$$

and $$D_{\mathrm{pq}}=(\phi_{\mathrm{p}m}\phi_{\mathrm{q}m}|\phi_{\mathrm{q}m-1}\phi_{\mathrm{q}m}). \quad (7)$$

Here V is the neutral core potential and we evaluate the transfer integral t^{pq}_{ij} by the extended Hückel method as

$$t^{\mathrm{pq}}_{ij}=KWS^{\mathrm{pq}}_{ij} \quad (8)$$

where W is the orbital energy of TCNQ, and we have used the value given by the photoemission experiment of -7.5 eV[14,24] and K is set equal to 1.2. Actually this choice is rather empirical as in the extended Hückel method where K is taken in the range of 1.0—2.0. We have also attempted to evaluate each term in the integral, namely the kinetic energy and the neutral core potential energy of the electron moving between p and q molecules, and they are found to be proportional to the overlap integral S^{pq}. The transfer integral t was also shown to be proportional to the overlap integral and it was nearly the same order of magnitude with the value estimated by Eq. 4. In the latter sections it will be seen that this choice is reasonable from a view of consistency of the spectral and magnetic properties of various complexes. In the actual calculation we have used the molecular orbital of Lowitz[21] for TCNQ$^-$ and the four term SCF-AO of Clementi *et al.*[25] The calculated overlap and transfer integrals are listed in Table 1.

The Coulomb repulsion energy U^{pp}_{mm} and U^{pq}_{mm} are those for the electrons on the same and the nearest neighbour sites, and they were calculated for a typical arrangement of the crystal by using Nishimoto-Mataga potential and the results are

$$U^{\mathrm{pp}}_{mm}=3.95\,\mathrm{eV} \text{ and } U^{\mathrm{pq}}_{mm}=2.29\,\mathrm{eV}.$$

The former value is the same with the value given by Hiroma, Kuroda and Akamatu.[26] The difference between these two terms is 1.66 eV, but the spectral analysis shows that it may be about 1.5 eV, therefore we estimate the screening effect of the electronic polarization[27] as being a factor of 0.9, and newly define the spectroscopic U value as

$$U=\eta(U^{\mathrm{pp}}_{mm}-U^{\mathrm{pq}}_{mm})=1.5\,\mathrm{eV} \quad (9)$$

where $\eta=0.9$. It appears that the η value is not so different for various crystals and it seems unlikely that η is very small and U is reduced to a great extent by the polarization of large conjugated molecules.

The Coulomb energy difference between the CT_2 and the ground configurations, which is important in the island type and the alternant type systems, may be written as U', where U' will be approximately given by

$$U'=U^{\mathrm{pq}}_{mm}-U^{\mathrm{pq+1}}_{mm}. \quad (10)$$

The numerical estimate of this small difference of energy may be a difficult problem, because it will require an accurate calculation including the Madelung energy of the crystal for two different configurations. Actually it may be either positive or negative values depending on the structure of the complex and it will give a measure of either the island or the alternant type configuration is stable in the ground state. Here we have empirically estimated the energy values from spectroscopic results to fit the calculated energy levels with the observed spectra, instead of evaluating this term by the calculation.

The last term D^{pq} means the interaction energy between the LE_1 and CT_1 configurations, and it is approximately estimated by the dipole-dipole interaction of the two transition dipoles. The size of the transition moment of the LE_1 band was estimated with the experimental data of solution spectra as 1.46 Å. The transition length for the CT_1 band was approximated as

Table 1. Molecular integrals of TCNQ complexes

		p q	i	j	S_{ij}^{pq}	t_{ij}^{pq}(eV)	D_{pq}(eV)
Rb–I	1:1	(−)—(−)′	m	$m-1$	0.0051	−0.0459	−0.3243
			m	m	0.0348	−0.3132	
		(−)—(−)″	m	$m-1$	0.0072	−0.0648	−0.0651
			m	m	0.0109	−0.0981	
Rb–II	1:1	(−)—(−)′	m	$m-1$	0.0100	−0.0900	−0.0860
			m	m	0.0083	−0.0747	
K	1:1	(−)—(−)′	m	$m-1$	0.0025	−0.0225	
			m	m	0.0301	−0.2709	
		(−)—(−)″	m	$m-1$	0.0054	−0.0486	
			m	m	0.0143	−0.1287	
Na	1:1	(−)—(−)′	m	$m-1$	0.0027	−0.0243	
			m	m	0.0298	−0.2682	
		(−)—(−)″	m	$m-1$	0.0057	−0.0513	
			m	m	0.0165	−0.1485	
Mor	1:1	(−)—(−)′	m	$m-1$	0.0021	−0.0189	
			m	m	0.0394	−0.3546	
TMB	1:1	(−)—(−)′	m	$m-1$	0.0128	−0.1152	
			m	m	0.0200	−0.1800	
TMA	2:3	(−)—(−)′	m	$m-1$	0.0029	−0.0261	
			m	m	0.0393	−0.3537	
Q	1:2	(0)—(−)	m	$m-1$	0.0124	−0.1116	−0.1871
			m	m	0.0153	−0.1377	
Ac	1:2	(0)—(−)	m	$m-1$	0.0110	−0.0990	−0.0701
			m	m	0.0067	−0.0603	
TMPD	1:2	(0)—(−)	m	$m-1$	0.0147	−0.1323	−0.0125
			m	m	0.0146	−0.1314	
		(−)—(0)′	m	$m-1$	0.0121	−0.1089	−0.0131
			m	m	0.0150	−0.1350	
TTF	1:1	(0)—(−)	m	$m-1$	0.0108	−0.0972	−0.1945
			m	m	0.0153	−0.1377	
NMP	1:1	(0)—(−)	m	$m-1$	0.0005	−0.0045	−0.1340
			m	m	0.0121	−0.1089	
Cs	2:3	(0)—(−)	m	$m-1$	0.0120	−0.1080	−0.1161
			m	m	0.0137	−0.1233	
		(−)—(−)′	m	$m-1$	0.0011	−0.0099	−0.2568
			m	m	0.0303	−0.2727	
Mor	2:3	(0)—(−)	m	$m-1$	0.0091	−0.0819	−0.1268
			m	m	0.0156	−0.1404	
		(−)—(−)′	m	$m-1$	0.0002	−0.0018	−0.2868
			m	m	0.0353	−0.3177	
MTPP	2:4	(0)—(−)	m	$m-1$	0.0133	−0.1197	−0.1450
			m	m	0.0184	−0.1656	
		(−)—(−)′	m	$m-1$	0.0097	−0.0873	−0.1442
			m	m	0.0183	−0.1647	
TEA	2:4	(0)—(−)	m	$m-1$	0.0145	−0.1305	−0.1008
			m	m	0.0164	−0.1476	
		(−)—(−)′	m	$m-1$	0.0145	−0.1305	−0.0178
			m	m	0.0127	−0.1143	
Bpy[a)]	2:4	(−)—(−)′	m	$m-1$	0.0157	−0.1413	
			m	m	0.0154	−0.1386	

a) (*N*,*N*′-Dibenzyl-4,4′-bipyridylium)$_2$ (TCNQ).

S_{mm}^{pq} R^{pq} and its center was placed in the midpoint of the two TCNQ molecules.

The energy level of the LE_1 is also important in spectral analysis, and it was estimated from the solution's spectral data as 1.5 eV and we denote it as Δ in the following formula. The calculation for the crystal was carried out with the model system, in which a possibly small unit to consider the interaction was selected. We have illustrated in Fig. 2 the unit by brackets and a translation unit by the square mark on the top.

For the dimer type system the configuration interaction between the ground, CT_1 and LE_1 levels must be considered. An approximate energy level scheme and wavefunctions obtained by the perturbational calculation are shown in Fig. 5. Numerical values of energy levels are calculated by diagonalizing the secular deter-

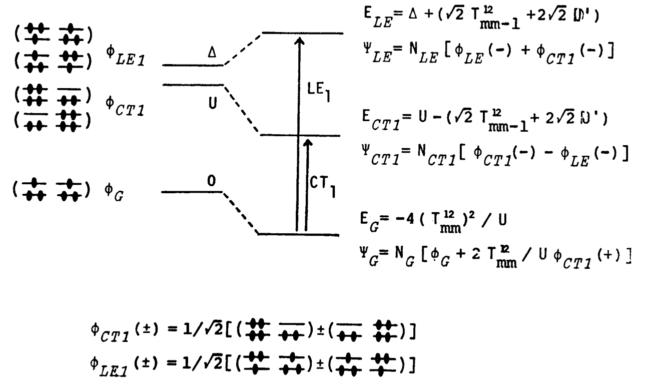


Fig. 5. Energy levels of a dimer type interaction. Actually the diagonal energy of CT_1 and LE_1 is nearly the same, namely $\Delta = \mathrm{U}$.

minant for the symmetrical and the antisymmetrical states. The secular equations are

$$\begin{array}{|ccc|l}
0 & 2t^{12}_{m.m} & 0 & \mathrm{G} \\
 & U & \sqrt{2}\,t^{12}_{m.m-1} & \mathrm{CT_1}^{(+)} \\
 & & \Delta & \mathrm{LE_1}^{(+)}
\end{array}$$
$$\begin{array}{|cc|l}
U & \sqrt{2}\,(t^{12}_{m.m-1}+2D^{12}) & \mathrm{CT_1}^{(-)} \\
 & \Delta & \mathrm{LE_1}^{(-)}
\end{array} \qquad (11)$$

where the off-diagonal energy values were estimated by the procedures mentioned above. The calculation was carried out for Rb(TCNQ)–I crystal, which has a dimer type configuration.[28] Also this model was applied for TMTTF (bis-tetramethylene-tetrathiafulvalene) because it may form dimer type crystal. The results of calculation are tabulated in Table 2 with with the observed spectral data. It is found that the agreements are fairly well for these crystals.

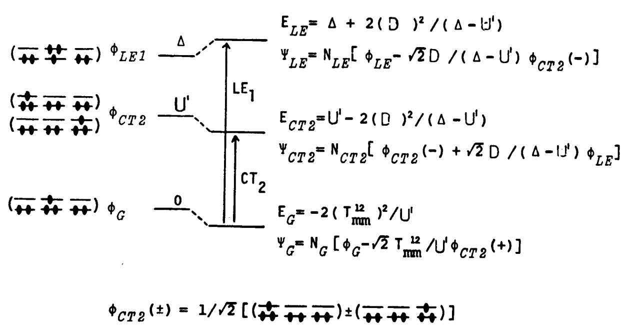


Fig. 6. Energy levels of an alternant type interaction.

For the dimer system the singlet ground state is stabilized to the triplet state, because the coupling of two neighbouring spins by the CT interaction is allowed for only the singlet state. The comparison of the calculated S–T separation energy with the magnetic susceptibility data will be given in the later section.

For the alternant system, the ground, the CT_2 and the LE_1 configurations were considered. An approximate solution by the perturbational treatment is illustrated in Fig. 6. The CT_2 level is not so close to the LE_1 level that the mixing between these configurations is not so significant. The secular determinants are as follows.

$$\begin{array}{|cc|l}
0 & \sqrt{2}\,t^{12}_{mm} & \mathrm{G} \\
 & U' & \mathrm{CT_2}^{(+)}
\end{array}$$
$$\begin{array}{|cc|l}
U' & -\sqrt{2}\,D^{12} & \mathrm{CT_2}^{(-)} \\
 & \Delta & \mathrm{LE_1}^{(-)}
\end{array} \qquad (12)$$

TABLE 2. ELECTRONIC ABSORPTION BANDS OF SEVERAL TCNQ COMPLEXES
Comparison of observed and calculated values.

	Type	CT$_2$				CT$_1$				LE$_1$			
		ΔE[a] Obsd (Calcd)	Intensity Calcd $f(\perp)$	Intensity Calcd $f(\parallel)$	Intensity Obsd ratio $(\perp/\parallel)$	ΔE[a] Obsd (Calcd)	Intensity Calcd $f(\perp)$	Intensity Calcd $f(\parallel)$	Intensity Obsd ratio $(\perp/\parallel)$	ΔE[a] Obsd (Calcd)	Intensity Calcd $f(\perp)$	Intensity Calcd $f(\parallel)$	Intensity Obsd ratio $(\perp/\parallel)$
Rb(TCNQ)–I	D					8.5 (8.5)	0.22	0.42	≈0.5	17.5 (19.8)	0.52	0.11	≈1.6
Q(TCNQ)$_2$	A	5.5 (6.1)	0	0.21	0					12.0 (13.1)	0	0.09	≈0
TTF(TCNQ)	A	3.0 (3.0)	0	0.28	0					12.0 (13.3)	0	0.08	0
TMTF(TCNQ)	D					≈4.0 (3.6)	0	0.18	0	18.0 (21.3)	0	0.08	0
NMP(TCNQ) (triclinic)	A	5.5 (5.5)	0.01	0.15	≈0					12.5 (12.7)	0.23	0.11	≈1.5
Cs$_2$(TCNQ)$_3$	I	6.0 (5.8)	0.002	0.18	0	11.0 (10.8)	0.08	0.52	0.1	17.7 (17.2)	0.13	0.08	3.5
Mor$_2$(TCNQ)$_3$	I	6.0 (6.4)	0.002	0.22	0	11.5 (11.5)	0.08	0.66	0.04	17.5 (17.9)	0.13	0.16	5.0
(MTPP)$_2$(TCNQ)$_4$	I	≈4.0 (4.0)	0.003	0.34	≈0	11.0 (11.1)	0.21	0.20	0.4	17.7 (15.9)	0.33	0.01	4.3
(TEA)$_2$(TCNQ)$_4$	I	≈4.0 (4.0)	0.001	0.27	0	11.0 (10.6)	0.13	0.11	0.5	17.7 (15.4)	0.19	0.001	3.6

[a] ΔE in $10^3\,\mathrm{cm}^{-1}$.

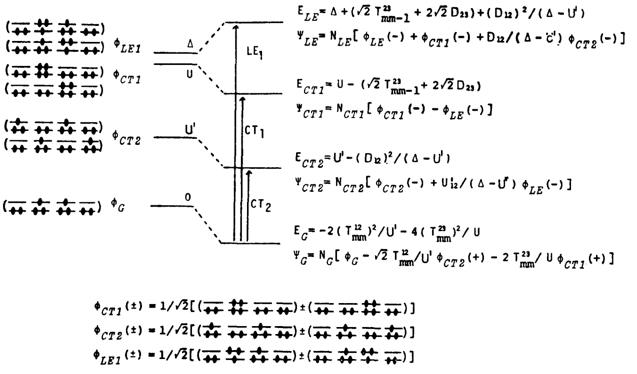


Fig. 7. Energy levels of an island type interaction. The diagonal energies are nearly the same for CT_1 and LE_1 states, namely $\Delta=U$.

The results of numerical calculation are shown for Q, TTF and the triclinic form of NMP–TCNQ crystals. The discussion on the calculated and the experimental results will be given for each crystals in the next section.

For the alternant system the spin correlation between the neighbouring sites can not be expected to be large, because the pairing scheme by the CT interaction between the nearest neighbour sites is not conceivable.

The island type system involves both the CT_1 and the CT_2 configurations and the calculation was carried out including these and LE_1 configurations. An approximate energy level scheme is given in Fig. 7. The numerical calculation was carried out with the secular equations given below.

$$\left|\begin{array}{cccc|l} 0 & \sqrt{2}t^{12}_{mm} & 2t^{23}_{mm} & 0 & G \\ & U' & 0 & -D^{12} & CT_2^{(+)} \\ & & U & \sqrt{2}t^{23}_{m,m-1} & CT_1^{(+)} \\ & & & \Delta & LE_1^{(+)} \end{array}\right| \qquad (13)$$

$$\left|\begin{array}{ccc|l} U' & 0 & -D^{12} & CT_2^{(-)} \\ & U & \sqrt{2}(t^{23}_{m.m-1}+2D^{23}) & CT_1^{(-)} \\ & & \Delta & LE_1^{(-)} \end{array}\right|$$

The results of calculations are shown in Table 2 for Cs, Mor, TEA, and MTPP–(TCNQ) complexes. Here the oscillator strengths of the electronic transitions are estimated for each transitions with reference to the stacking axis of TCNQ columns and they are given by *f*-numbers parallel and perpendicular to the stacking axis. It is found that the mixing of the CT_1 level with the LE_1 level gives significant changes of the polarization character guessed by the oriented gas model. The comparison of the calculated results with the experimental results will be given in the later section.

All calculations were performed at the Computation Center of Nagoya University.

Interpretation of Crystalline Spectra

Rb(TCNQ)-I. The crystalline structure of Rb(TCNQ)-I was analyzed by Hoekstra, Spoelder and Vos[28] and the crystals have monoclinic symmetry with the space group $P2_1/c$. The projection of molecules onto the developed crystalline plane is shown in Fig. 8, where the TCNQ ions form rows along the a-axis and the interplanar distances show alternation of 3.159 Å and 3.484 Å, which implies that dimeric pairs are formed in the crystals. The crystalline absorption spectra were measured along the a- and b-axes of the (001) plane, and are shown in Fig. 9. The lowest energy transition is regarded as the CT_1 transition, and its energy and the polarization ratio are in fairly good agreement with the calculated results. The LE_1 band of $(TCNQ)^-$ shifts to the higher energy region by 3000—4000 cm^{-1}, and it seems that the blue shift of the LE_1 band is a characteristic of the dimer type electron configuration of TCNQ complex crystals. The calculated results of the energy and the polarization ratio of the LE_1 band are not in perfect, but in farily good agreement with the observed tendency of the spectra. The blue sflift of the LE_1 band is interpreted as the mixing of the CT_1 and the LE_1 levels. The third transition at 26000 cm^{-1} region may be reasonably assigned to the second band of $(TCNQ)^-$, namely the LE_2 band, because the second band of $(TCNQ)^-$ in acetonitrile solution appears at 24000 cm^{-1}.

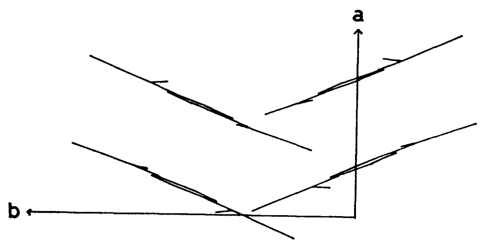


Fig. 8. Projection of Rb(TCNQ)-I onto the developed (001) plane.

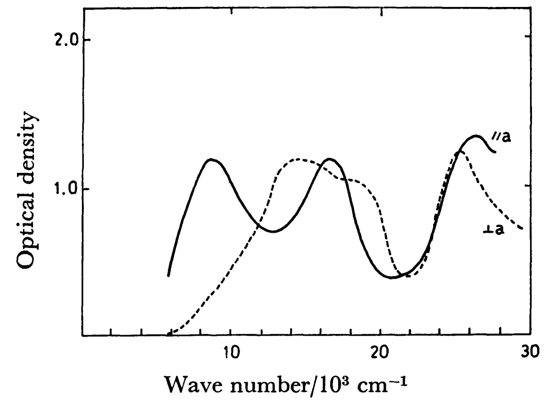


Fig. 9. Polarized absorption spectra on the (001) plane of a single crystal of Rb(TCNQ)-I.
——: a axis, ……: b axis.

The peaks of main absorption bands are in reasonable agreement with the powder spectra given by Sakai *et al.*[29] and Oohashi and Sakata,[30] and the polarized spectra presented here give an evidence of the CT character of the lowest energy transition.

Q(TCNQ)₂. The crystalline structure of Q-$(TCNQ)_2$ was analyzed by Kobayashi, Marumo and Saito[8] and the projection of molecules onto the developed (100) plane is shown in Fig. 10. The structure is disordered as regard to the orientation of quinolinium ions. The crystalline absorption spectra were measured with the (100) plane with the light polarized

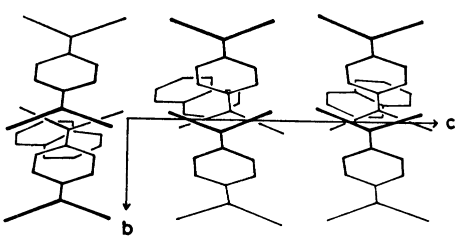


Fig. 10. Projection of Q(TCNQ)$_2$ onto the developed (100) plane.

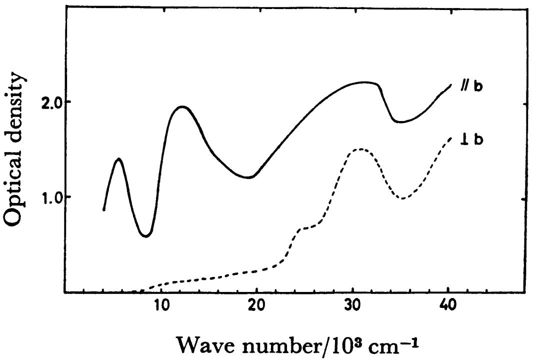


Fig. 11. Polarized absorption spectra on the (100) plane of a single crystal of Q(TCNQ)$_2$.
——: b axis, ······: c axis.

parallel to the b- and c-axis and the spectra are shown in Fig. 11. The spectra are typical of the alternant type structure that the CT$_2$ transition is at the lowest energy region and the LE$_1$ band is not shifted to the higher energy region. Namely the CT$_2$ band is observed at about 5500 cm^{-1} and the LE$_1$ band is found at 12000 cm^{-1}. The LE$_1$ band is not shifted because the mixing of the CT$_2$ and the LE$_1$ levels is not so significant, for the diagonal energy values of the CT$_2$ level is much less than that of the LE$_1$ level. The energy of the CT$_2$ level is certainly smaller than that of the CT$_1$ level and we have estimated the U' value for this crystal at 0.8 eV, which is much smaller than the U value of 1.5 eV of the dimer system. The results of calculation are shown in Table 2 and it is seen that the observed and calculated results are in fairly good agreement. It will mean that the assumed alternant model is reasonable to interpret the electronic spectra of this crystal.

The absorption bands at above 26000 cm^{-1} region along the b-axis may be due to the LE$_2$ state and the first excited state of neutral TCNQ molecule and the band found at 31000 cm^{-1} may be ascribed to the local transition of the quinolinium cation. The appearance of the LE$_1$ band at lower energy region at about 12000 cm^{-1} implies that the electronic configuration of TCNQ column is an alternant type. This criterion may be used for the analysis of the spectra of other TCNQ complex crystals.

TTF(TCNQ). The crystal of TTF(TCNQ) is the best conducting organic complex hitherto known[4,31–34] and the optical spectra have been intensively investigated by several groups.[35–37] The present result provides a polarization measurement in the near infrared and visible region by the transmission measurement, therefore it may be interesting to compare the result with the former investigations by other methods.

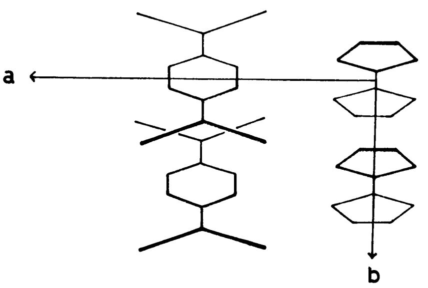


Fig. 12. Projection of (TTF) (TCNQ) onto the developed (001) plane.

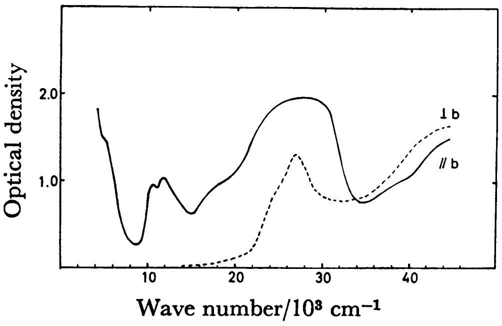


Fig. 13. Polarized absorption spectra on the (001) plane of a single crystal of (TTF) (TCNQ).
——: b axis, ······: a axis.

The crystalline structure of the complex was analyzed by Kistenmacher, Phillips and Cowan[11] at room temperature and by Blessing and Coppens[12] at low temperature. The projection of molecules onto the (001) plane is shown in Fig. 12. Both TCNQ and TTF form independent segregated columns along the b-axis. The CT transition will be particularly polarized along this axis, and actually it is found that the absorption edge of the CT band is observed along the b-axis (Fig. 13). The maximum of this band could not be found by the transmission method, because it was in the out of the range of the present spectrophotometric system.

The peak of this transition was observed by Torrance *et al.*[37] with a powdered sample at 3000 cm^{-1}, while Jacobsen, Tarner, Garito and Heeger[36] measured the reflectivity of the single crystal from 4000 cm^{-1} down to 50 cm^{-1} and found that the maximum of conductivity lies at 1300 cm^{-1}. We also measured the single crystal reflectivity from 35000 cm^{-1} to 4000 cm^{-1}, and confirmed the result of Grant *et al.*,[35] and by combining this result with the infrared data of Jacobsen *et al.* we calculated the absorption maximum by Kramers-Kronig transformation to be at 3000 cm^{-1}.[38] The peak of absorption is located at 3000 cm^{-1}, therefore the character of this transition is assigned as the CT$_2$ type by the analogy with the spectra of other complexes. The CT band is observed at the lowest energy region and the LE$_1$ band is appeared at 12000 cm^{-1} without any blue-shift, hence the electron configuration of TTF(TCNQ) will be an alternant type, or at least an alternant type mixed with an island type. The mixing of an island type with an alternant type is an important feature of the present crystal, and anyhow it implies that an electron transfer from TTF to TCNQ is incomplete.

The theoretical calculation of the energy level is carried out by the alternant model with the U' value of 0.35 eV and the result is in satisfactory agreement with the observed energy, the intensity and the polarization ratio of both the CT_2 and LE_1 bands. In spite of this, the spectral feature of this complex is very close to other island type crystals, therefore the basic electron configuration may involve an island type. Then, in addition to the CT_2 band, the CT_1 and LE_1 bands will be mixed, but this type of mixing could not be confirmed distinctly in the present spectra. Namely, the band at 18000 cm^{-1} region along the b-axis may be a shifted LE_1 band mixed with the CT_1 band in the island model, however, the TTF cation may absorb in this region along this direction, because it has own absorption bands at 18000, 23000, 29000, and 40000 cm^{-1}.[39] A recent unpublished result by Torrance and coworkers[40] gave absorption bands in TTF–$Br_{0.76}$ at 5000, 13000, and 18000 cm^{-1}, but the intensities were smaller than that of TCNQ anion. Therefore the band appearing at 18000 cm^{-1} along the b-axis is reasonably considered to be a mixed CT_1 and LE_1 bands. Thus the spectral results support a strong mixing of the alternant and the island type.

In addition to this, the broad absorption bands around 24000—30000 cm^{-1} region are ascribed to the negative and neutral TCNQ species, because the maximum of these absorptions are expected at 24000 and 25000 cm^{-1}, respectively. These are another reasons to assign the electron configuration of this crystal to the mixed alternant and island types.

Following the theoretical calculation the ground state is represented by 0.91 $\varphi_A+0.41\ \varphi_I$, where the starting set is a pure alternant configuration, and it means that the electron configuration is 83% of the alternant and 17% of the island type. Then extra neutral vacant sites are produced adjacent to the island site, and if these sites were filled by further electrons from the donor molecule, then the amount of charge transfer will be 0.585. For this population, the ground state is written as 50% of the alternant and 50% of the island configurations, which is in perfect agreement with the spectral properties discussed above.

There are several evidences[12–15] that an electron transfer from TTF to TCNQ is not complete, and the present results give another evidences that both TCNQ and TTF columns are partially ionized and the excess charges may delocalize or fluctuate within or between columns. This view may give an important clue to the understanding of this particular complex.

Of course, other interpretations on the spectral propeties of TTF(TCNQ) have been presented by the metallic band model[4,36,41] or the polaron theory,[42] but our approach is based on a molecular model, which may give wide correlations with other TCNQ complexes.

TMTF(TCNQ). Ueno, *et al.*[43] have synthesized bi(4,5-tetramethylene-1,3-dithiol-2-ylidene), (TMTF), which is an analogue of TTF, and prepared its complex with TCNQ and kindly gifted us the crystals. We have measured and compared the spectral property with that of TTF(TCNQ). The crystalline data of TMTF-(TCNQ) was examined and it was found that the crystal is triclinic and the lattice constants are a=7.07, b=13.39 and c=6.91 Å and α=70.9, β=105.0 and γ=93.0°. The crystalline absorption spectra were measured along the a- and c-axis, and the CT band was found along the a-axis with a maximum at 5500 cm^{-1} (Fig. 14). The LE_1 band was also found along the a-axis with a maximum at 17400—19500 cm^{-1}. Although the crystalline structure of the complex is not yet determined, the structure of the crystal may be supposed that the stacking axis of $(TCNQ)^-$ is along the a-axis. The appearance of the LE_1 band at higher energy region indicates that the interaction between the CT_1 level and the LE_1 level in the dimer or in the linear chain structure may be very strong in this crystal. Actually the calculated values of transition energies for the dimeric system of TTF(TCNQ) are very close to the experimental values found for TMTF(TCNQ) (Table 2). From these analysis it is supposed that the electronic structure of TCNQ in this crystal will be all negatively charged with a dimeric or a linear chain structure. However, another possibility that the crystal may have a D^+A^- type structure may remain because the crystal structure is not yet determined.

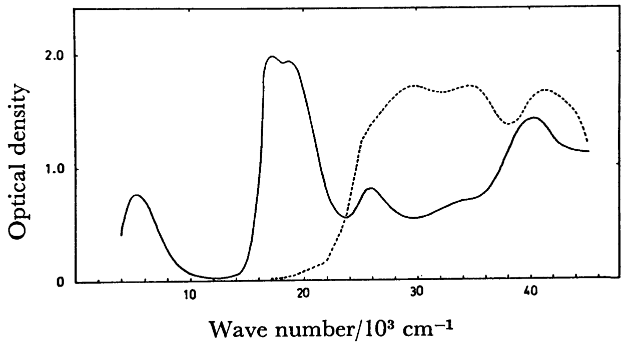


Fig. 14. Polarized absorption spectra on the (010) plane of a single crystal of (TMTF) (TCNQ).
——: a axis, ······: c axis.

NMP(TCNQ). Two crystalline forms of NMP-(TCNQ) have been reported[44] and the crystalline structure analysis have been carried out only for the good conducting triclinic system by Fritchie[45] and recently by Kobayashi.[46] It has been shown that columns of both TCNQ and NMP develop parallel to the a-axis in the triclinic crystal.

Both the monoclinic and the triclinic crystals were prepared from the same acetonitrile solution, and they were distinguished by the color on transmission or reflection. Their developed faces were confirmed by taking the X-ray photographs and they were (001) plane for the triclinic and (100) plane for the monoclinic crystals. The projection of molecules onto the (001) plane of the triclinic crystal is shown in Fig. 15. Following the crystal structure analysis, it has been presumed that the crystal contains only $(TCNQ)^-$ and $(NMP)^+$ species, but the explanation on the magnetic susceptibility of this crystal[2,47] may be difficult by a fully charged and stacked model. Soos has suggested a model that TCNQ column may contain some neutral

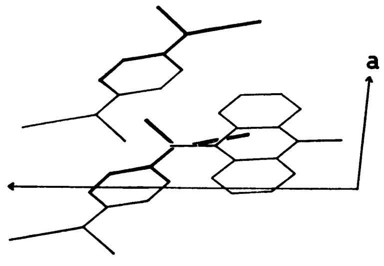


Fig. 15. Projection of triclinic (NMP) (TCNQ) onto the developed (001) plane.

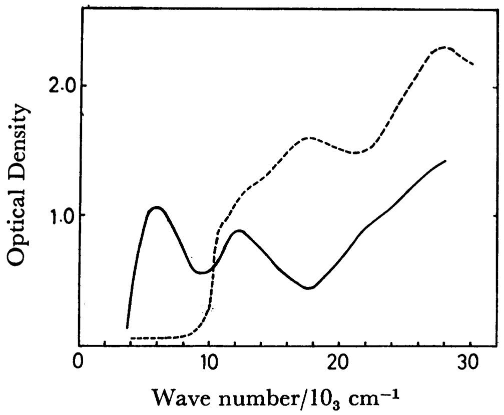


Fig. 16. Polarized absorption spectra on the (001) plane of a single crystal of triclinic (NMP)(TCNQ).
——: a axis, ······: b axis.

species to explain several physical properties.

The spectra measured with the triclinic crystal for the (001) plane are shown in Fig. 16, and it is easily found that the CT band appears solely along the a-axis at 5500 cm^{-1}, and the LE_1 band is observed at about 12000 cm^{-1}. This result is a typical pattern of an alternant electron configuration, namely excess electrons exist on alternate TCNQ sites. It may mean that an electron transfer from $(TCNQ)^-$ to $(NMP)^+$ may occur at almost every alternate TCNQ sites. By this transfer a half of $(NMP)^+$ ions will become neutral radicals, and the absorption band at 17000 cm^{-1} region may be assigned as due to the neutral radicals, since Sakata and Nagakura[48] have found the absorption in this region with neutral radicals. It seems that NMP radicals also take alternate configurations, since if the radicals are paired another strong band should appear at 13000 cm^{-1} region, but it is not clearly found in the spectra.

The result of theoretical calculation by the alternant model with the U' value of 0.7 eV is in good agreement with the spectra of the triclinic crystal. The CT band appearing at 5500 cm^{-1} is interpreted on this basis as a CT_2 band. The dichroic intensity ratio for the CT_2 and LE_1 bands are satisfactorily explained, and the broad bands appearing at 12000 cm^{-1} region along the a- and b-axis are assigned to the LE_1 band. The absorption bands around 26000—28000 cm^{-1} region are assigned as the superposed TCNQ neutral and ionic species. A recent reflectivity measurement of this crystal provides an evidence of the presence of neutral TCNQ species.[38]

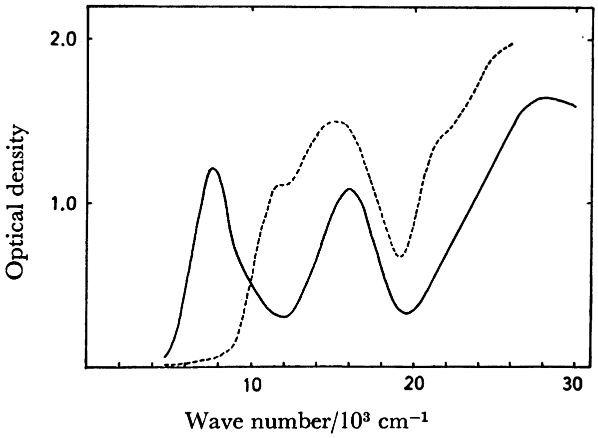


Fig. 17. Polarized absorption spectra on the (100) plane of a single crystal of monoclinic (NMP) (TCNQ).
——: b axis, ······: a axis.

The crystalline absorption spectra of the monoclinic form were measured with the (100) plane, and the CT band was found at higher energy than for the triclinic crystal (Fig. 17). The LE_1 band is blue shifted. Although the crystalline structure of this form has not yet been published,[44] but it is suggested to be composed of D^+A^- stacks. Then the spectral result is explained in such a way that the lowest energy transition is a CT between $(TCNQ)^-$ and $(NMP)^+$, and the bands at 12000 and 16000 cm^{-1} are the LE bands of $(TCNQ)^-$ and $(NMP)^+$, respectively. A nearly diamagnetic behaviour of this crystal[44] will be also consistent with the D^+A^- model of this crystal.

Thus the variation of the physical properties of the triclinic and the monoclinic NMP(TCNQ) is reasonably explained by the change of the electron configuration of the crystals.

$Cs_2(TCNQ)_3$. The crystalline structure was determined by Fritchie and Arthur.[16] It belongs to a monoclinic system of the space group $P2_1/c$. One of the TCNQ in the unit cell is situated on the center of symmetry and is considered as neutral, and other two non-centric TCNQ are analyzed to have negative charges. The localization of the charge is also confirmed by the photoemission spectroscopy.[49] The projection of molecules onto the developed crystalline plane is shown in Fig. 18. The TCNQ column elongates along the b-axis with interplanar spacings of 3.22 Å for adjacent charged molecules. In Fig. 3 the overlap for charged species is shown to be larger than for the mixed species.[3] Since the center of TCNQ molecules are lined along the b-axis, the CT bands may be observed particularly along the b-axis, if the mixing of the CT and LE_1 levels is not significant. Also the long-axis of TCNQ is inclined 45° to the b-axis, therefore the LE type bands are expected to give the dichroic intensity ratio of 1 : 1 for the b- and a-axis.

The crystalline absorption spectra have been measured before by Hiroma *et al.*,[26] but we have measured again to extend into near infrared and the spectra with the (001) plane are shown in Fig. 19. Two CT bands found at 6000 and 11000 cm^{-1} mainly along the b-axis. The lower energy band is considered as the CT_2 type

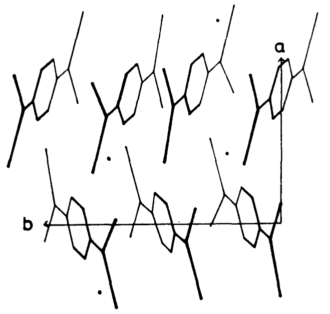


Fig. 18. Projection of $Cs_2(TCNQ)_3$ into the developed (001) plane.

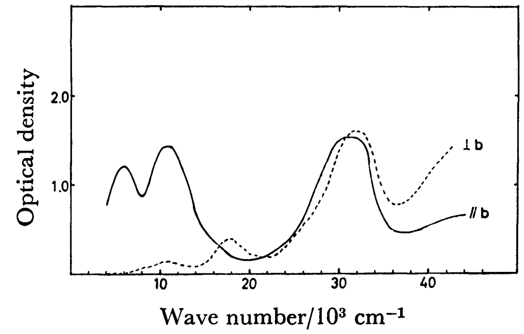


Fig. 19. Polarized absorption spectra on the (001) plane of a single crystal of $Cs_2(TCNQ)_3$.
——: b axis, ······: a axis.

between the neutral and charged TCNQ molecules, and the higher energy one is the CT_1 band mixed to some extent with the LE_1 band. The mixing between these two transitions is verified by a theoretical calculation. The blue shift of the LE_1 band is as much as 5000 cm^{-1}, and the change of the intensity is very remarkable, and these characteristics are reasonably explained by the interaction of the CT_1 and LE_1 levels. The deviation of the observed intensity ratio (3.5) from the oriented gas model (1.0) is also accounted for by this calculation as the effect of the mixing of the CT_1 and LE_1 levels. The observed dichroic ratio for the LE_2 band (1.06) is in good agreement with the oriented gas model (1.0) because the LE_2 level is not significantly influenced by other levels except that the band is blue shifted by 2000 cm^{-1}.

The characteristic of the island type electron configuration is exemplified with these spectra that both the CT_2 and CT_1 bands are observed along the stacking axis of TCNQ columns; the LE_1 band is blue shifted and the dichroic intensity ratio are changed from the oriented gas model by the interaction of the CT_1 and LE_1 levels.

$(Mor)_2(TCNQ)_3$. The crystal structure of $(morpholinium)_2(TCNQ)_3$ was determined by Sundaresan and Wallwork[50]; the crystals are monoclinic, belonging to the space group $P2_1/c$. Two of three TCNQ species in the unit cell are negatively charged, while the other TCNQ is neutral. The overlapping of the charged molecules and the charged and neutral molecules are shown in Fig. 3, and the patterns are similar to other systems having the same charge distributions.[3]

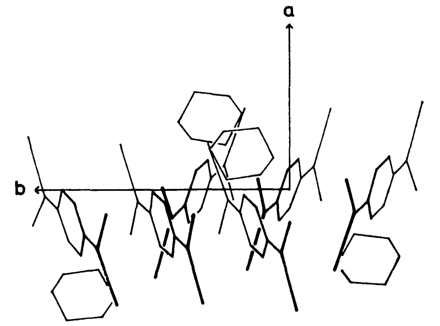


Fig. 20. Projection of $(Mor)_2(TCNQ)_3$ onto the developed plane.

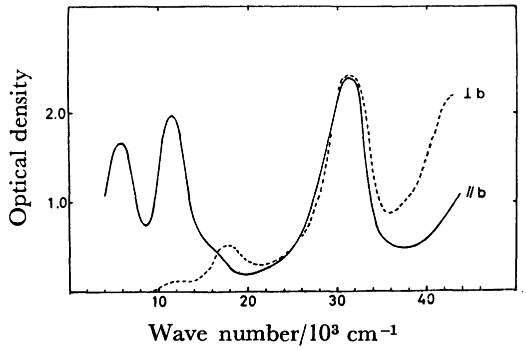


Fig. 21. Polarized absorption spectra on the (001) plane of a single crystal of $(Mor)_2(TCNQ)_3$.
——: b axis, ······: a axis.

The crystalline absorption spectra were measured with the (001) plane and the projection of molecules onto this plane is shown in Fig. 20. The column of TCNQ elongates along the b-axis, and the long-axis of TCNQ molecule is inclined to the b-axis by 45°. The spectra are shown in Fig. 21 and two CT bands are clearly observed along the b-axis with maximum at 6000 and 11500 cm^{-1}. The band at 6000 cm^{-1} is assigned to the CT_2 band, the band at 11500 cm^{-1} is the CT_1 mixed with the LE_1 band. The LE_1 band is found at 17500 cm^{-1}; it is blue shifted as much as 5000 cm^{-1}. The dichroic intensity ratio of the LE_1 band is also changed from the oriented gas model of 1.0 to 3.0. On the other hand the LE_2 band shows the same intensity for the b- and a-axis in accordance with the oriented gas model.

The observed energies and the polarization characteristics are well explained by a theoretical calculation with an island model, and it is very interesting that a gross feature of the spectra is very close to the spectra of $Cs_2(TCNQ)_3$ in spite of a great difference in chemical nature of the cationic group. It will mean that the crystalline spectra reflect the electron configuration of the crystal.

$(TEA)_2(TCNQ)_4$. The crystal structure of triethylammonium TCNQ complex was determined by Kobayashi, Ohashi, Marumo and Saito;[17] the crystal is triclinic with space group $P\bar{1}$, and four TCNQ molecules form a repeating unit in the column. Two of four TCNQ molecules in the centrosymmetric inside pair are considered to have negative charges and two

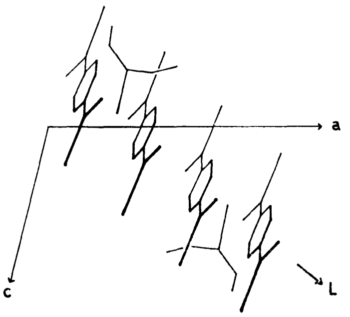


Fig. 22. Projection of $(TEA)_2(TCNQ)_4$ onto the developed (010) plane.

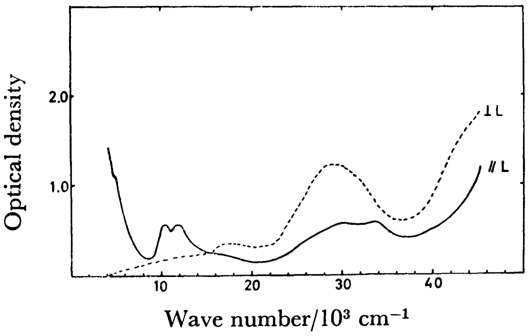


Fig. 23. Polarized absorption spectra on the (010) plane of a single crystal of $(TEA)_2(TCNQ)_4$
——: Parallel to the stacking axis, L,
……: perpendicular to the stacking axis.

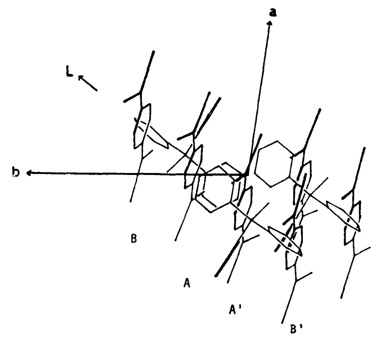


Fig. 24. Projection of $(MTPP)_2(TCNQ)_4$ onto the developed (001) plane.

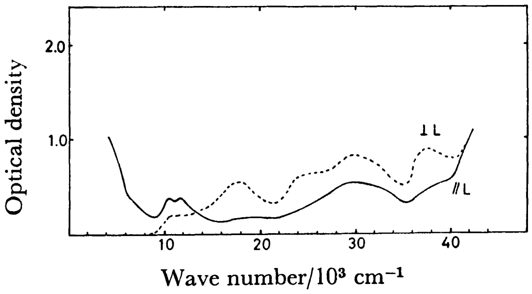


Fig. 25. Polarized absorption spectra on the (001) plane of a single crystal of $(MTPP)_2(TCNQ)_4$.
——: Parallel to the stacking axis, L,
……: perpendicular to the stacking axis.

outer TCNQ molecules are thought to be neutral. Thus the structure is typical of an island type configuration. The stacking axis of TCNQ column makes about 40° to the a-axis in the (010) projection, and the long-axis of the TCNQ molecule makes 50° to the stacking axis (Fig. 22). On this projection the LE_1 and LE_2 bands are expected to give a dichroic intensity ratio of 1.4 with the stacking axis $(I_\perp/I_{//})$.

The crystalline absorption spectra measured with the (010) plane in the direction parallel and perpendicular to the stacking-axis are shown in Fig. 23. Along the stacking axis prominent absorptions are found at around 4000 and at 11000 cm^{-1}, and two bands are observed at 17700 and 29000 cm^{-1}. Although the maximum of the lowest energy band is not found, but it is unambiguously assigned to the CT_2 band because of its polarization, and the next band at 11000 cm^{-1} is a transition to the coupled LE_1 and CT_1 states. Another coupled transition of the CT_1 and LE_1 states is found at 17700 cm^{-1}. The energy levels, the intensities and the dichroic ratio of these transitions are well explained by the theoretical calculation as a consequence of the mxing of the LE_1 and CT_1 levels. The distribution of intensities between these two bands and the change of the dichroic ratio suggests that the mixing is very efficient between these two levels. The pattern of the spectra may be typical of 2 : 4 type island electron configuration, in which negatively charged TCNQ species are surrounded by neutral TCNQ molecules. The CT_2 band may have lower energy than that of 2 : 3 type system, because the electron correlation between the neighbour sites is much reduced by a presence of the extra neutral TCNQ molecule. The absorption bands at 28000—30000 cm^{-1} are assigned to the LE_2 bands of $(TCNQ)^-$ and (TCNQ), and the dichroic ratio is about 2.0, which is in fairly good agreement with the oriented gas ratio.

$(MTPP)_2(TCNQ)_4$. The crystalline structure of methyltriphenylphosphonium TCNQ was determined by McPhail, Semeniuk and Chesnut,[51] and by Konno and Saito.[52] The crystal belongs to a triclinic system with the space group of $P\bar{1}$. The tetrad structure was found for TCNQ column, but the standard deviation for the bond distances are larger than the difference of bond distances of $(TCNQ)^0$ and $(TCNQ)^-$. The crystalline absorption spectra were measured with the (001) plane, and the projection of molecules onto this plane is shown in Fig. 24. The stacking axis of TCNQ makes about 45° to the b-axis on this projection, and the long-axis of the TCNQ molecule is inclined about 50° to the stacking axis of TCNQ column.

The spectra shown in Fig. 25 are very close to that of $(TEA)_2(TCNQ)_4$, therefore it seems more probable that the electrons are localized within two TCNQ molecules rather than that they delocalize over the column. The lowest energy absorption was found around 4000 cm^{-1} region along the stacking axis, and it is assigned to the CT_2 band. Two prominent peaks were observed at 11000 and 17700 cm^{-1} region and these are regarded as the transitions to the mixed LE_1 and CT_1 states. The observed energy values and the dichroic intensity ratios are well accounted for by the theoretical calculation based on the island model. The LE_2 band appears at 25000 and 30000 cm^{-1} region, and this splitting will imply that the TCNQ species exist as negative and neutral ones in the crystal.

The spectral similarity between $(TEA)_2$- and $(MTPP)_2(TCNQ)_4$ is very striking that a similar electron configuration of TCNQ column is supposed for these chemically different crystals. Among four TCNQ molecules labelled by A, A′, B and B′ in Fig. 24,[51] the spectral, magnetic and a slight variation of bond length support that electrons may be localized on A and A′ sites, but the mode of overlapping may not be in favour of this assignment.

Energy Separation of the Triplet and Singlet States

The magnetic susceptibilities of TCNQ complexes have been measured for various crystals by many people, and experimental data of the energy separations for the triplet and singlet states have been accumulated.[1,5] The singlet state of the coupled TCNQ dimers will be stabilized by the CT interaction as compared to the triplet state, because the CT interaction could not be expected for the triplet state because of Pauli principle.[52] Following the perturbational calculation given in the previous section, the singlet state of the dimer will be stabilized to the triplet state approximately by

$$J = \frac{4t_{mm}^2}{U} \qquad (14)$$

where U is the spectroscopic electron correlation energy, and t_{mm} is the transfer integral between the half-filled highest occupied orbitals. Although there may be a slight change of U values depending on the crystalline structure and the electron configuration, but we may take it as a constant value of 1.5 eV. The J values are calculated by Eq. 14 for several complexes which have TCNQ pairs and the results are shown in Table 3. The experimental J values are estimated by the temperature dependence of the magnetic susceptibility. It is seen that the agreement between the experimental and the calculated J values is reasonably good in spite of a simple model used for the calculation. Although the structure of the alkaline salts of TCNQ are not dimeric in a rigorous sense,[5] as in their low temperature phase another neighbour site is found close to the dimer pair.[18,19] In spite of this the magnitude of the second transfer integral t_2 is one third of the dimer pair, so we have ignored this effect in this treatment.

Table 3. Calculated and observed magnetic J values

	J-values (eV)		Reference	
	Calcd	Obsd	Magnetic data	Crystal structure
Rb-I	0.27	0.28	56	28
Na	0.19	0.16	57	18
K	0.19	0.25	56	19
Mor (1:1)	0.34	0.36	58	63
TMA	0.33	>0.2	59	64
TMB[a]	0.11	0.20	56	65
Mor (2:3)	0.27	0.31	58	50
Cs (2:3)	0.19	0.16	60	16
TEA (2:4)	0.032	0.034	61	16
MTPP (2:4)	0.068	0.065	61	51
BPY (2:4)	0.05	0.05—0.072	62	66
TTF (>60°K)	b)	b)	53, 54	11, 12

a) (1,2,3-Trimethylbenzimidazolium)-(TCNQ).
b) See text.

For the alternant type crystal the stabilization by the charge transfer effect may be small since the CT interaction can not be expected as the first order effect. In fact very small J values were found NMP, Q and Ac–TCNQ complexes.[2] These results may be well explained by the model that these crystals have the alternant electron configuration, and the CT type stabilization may not occur significantly.

The susceptibility of the TTF–TCNQ crystal behaves differently from other good conducting crystals; it shows a distinct temperature dependence even in the metallic state.[53,54] In view of an importance of accurate susceptibility data[53] for the analysis of the electronic structure of the crystal, we have attempted to fit the calculated susceptibility by our model with the observed one, although there remain several parameters which may be checked by other methods. The susceptibility will be particularly dependent on the number of active spins, therefore the number of electron transfer may be guessed by this work.

The calculation of transfer integrals in and between the TTF and TCNQ chains were carried out by Berlinsky *et al.*,[24] and by using their values we may estimate the CT interaction between the chains as being negligible and that within the TTF chain is 0.007 or 0.086 eV depending on either sulphur 3p or 3d orbitals being used. For the TCNQ chain, we have used our own integral values, and the S–T separation is estimated as 0.052 eV. In order to simplify the calculation, the dimeric state in TTF chain is also assumed to have the same activation energy of 0.052 eV. Then the spins on the TCNQ and TTF chains are divided into the island and alternant type and the number of the transferred electron and their distributions are adjusted to fit the calculated curve with the observed one. The susceptibility was calculated by using the dimer model for the island system and Heisenberg model[55] for the alternant system. The best fits were obtained by using the following set of parameters: Case 1. TCNQ chain, alternant 0.25 (J=0.024 eV), island 0.335 (J=0.052 eV); TTF chain, alternant 0.17 (J=0.008 eV), island 0.415 (J=0.052 eV), the number of electron transfer is 0.585; Case 2. TCNQ chain, alternant 0.48 (J=0.021 eV), island 0.11 (J=0.052 eV); TTF chain, alternant 0.10 (J=0.010 eV), island 0.49 (J=0.052 eV), the number of electron transfer is 0.59. By these parameters the observed curve was reproduced with the error less than 10%.

We have completely ignored the interaction between the spins on the island and alternant system within the chain, and actually the interaction of these clusters may not be simple enough to allow such a simple treatment. The ratio of the alternant and the island system were not exactly the same in TCNQ chain by both parameters, but it is roughly in agreement with the analysis presented in the previous section. Moreover the number of charge transfer is in good agreement with the X-ray result of Coppens (0.48—0.60).[13] The number of charge transfer may vary with temperature, but such a consideration was not included in this calculation.

Electrical Conductivity and Electronic Structure

Variety of TCNQ complexes may be classified into several groups from the electrical conductivity[2,67]; (a) the low conductive group which are nearly insulating or semiconducting with high activation energies, (b) the intermediate case which are semiconducting with small activation energies, and (c) the good conducting ones which behave like metal.

Alkaline salts of 1 : 1 composition, which may form the dimer type crystals, and several island type crystals which have localized electrons belong to class (a).[67] Following the one-electron band theory[5] the high resistivity will be explained by the band gap produced by the Peierls transition at low temperatures.

According to Ovchinikov,[68] the band gap in the one-dimensional Hubbard model is given by $U-4t$, and we may compare the observed activation energies of various crystals with the estimated activation energies given by

$$\Delta E = \frac{1}{2}(U-4t) \tag{15}$$

Here t values are given in Table 1 and we take an average of two nearest neighbour values and the results of the calculation are tabulated in Table 4. The agreement between the calculated and the experimental values is not so bad for these crystals. From a view of the Mott theory[69] on the metal to insulator transition, we may compare $4t$ values for several crystals with U values. It gives $U>4t$ for most crystals, therefore the metallic state will not be easily realized. The smallest U' values is 0.35 eV of TTF(TCNQ), therefore the small U' is apparently in favour of the metallic state, but still the inter- and intra-site Coulomb energies are by no means negligible. The transfer integrals are in the range of 0.35—0.10 eV, and it is larger for the dimer type configuration than the alternant or the island type, but U is larger again for the dimer type.

Suezaki[70] has calculated the conductivity of TCNQ complexes by the Hubbard Hamiltonian, and has proposed a formula that

$$\sigma = \sigma_0 e^{-\Delta E/kT}$$

$$\sigma_0 = \frac{1}{12\pi}\,\frac{e^2 n\delta^2}{\hbar}\,\frac{t}{U} \tag{16}$$

where δ is the vector connecting between two TCNQ molecules. We have evaluated by using our t and U values for $(TEA)_2(TCNQ)_4$, and σ_0 is estimated as $8\,\Omega^{-1}\,cm^{-1}$ for the b-axis, which is a reasonable fit as compared to the observed value of $4\,\Omega^{-1}\,cm^{-1}$.[67] However, the same formula applied to $(MTPP)_2$-$(TCNQ)_4$ and $Cs_2(TCNQ)_3$[67] gives the results which are two or three orders of magnitudes larger than the experimental values. For $Q(TCNQ)_2$ the calculated one is one or two orders of magnitudes smaller than the observed values,[67,71] therefore this formula may be limited for explaining the electrical properties of these complexes.

Table 4. Activation energies for semiconductivity

	ΔE(eV) Calcd	ΔE(eV) Obsd	References
Na	0.33	0.33	67
K	0.35	0.35	67
Rb–I	0.35	0.49	82
Rb–II	0.60	0.17	82

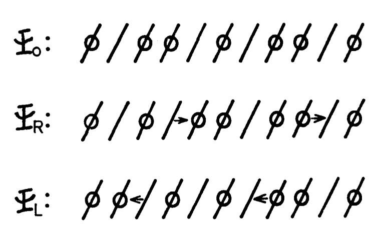


Fig. 26. Basic electron configurations of TTF(TCNQ). The top row represents the ground state without field (Ψ_0). The middle row shows an electron flowed into the right (Ψ_R), and the bottom row exhibits a flow into the opposite direct on (Ψ_L).

All good conducting TCNQ complexes like Q, NMP, Ac and TTF(TCNQ) have alternant electron configuration as a basic unit; in addition, they have a common characteristic that the cation groups are stacked to form their own columns. It seems certain that the cation stack also plays an important role in the conduction mechanism. For example, the TTF column may be even more conductive than TCNQ column,[54] however, not all TTF complexes show good conductivity,[72] therefore the correlation of motion of electrons and holes on both chains may be very significant. Bloch *et al.*[73] discussed this point from a band theory, and suggested that the overlapping of the energy levels of the donor and the acceptor bands is important. A partial electron transfer from the donor to acceptor column may be realized by such a band scheme.

We have tried to estimate the conductivity based on our model of TTF(TCNQ). The basic electron configuration of TCNQ column in this particular crystal is written by an admixture of an island and an alternant type as is explained in the previous section. The ground state wavefunction for the column will be given by

$$\psi_0 = a\varphi_A + b\varphi_I \tag{17}$$

and the basic electron configurations are depicted in Fig. 26. The coefficients a and b may be estimated from the spectral and structural analyses as mentioned before.

By applying the electric field $\boldsymbol{E}$, one of the electron in the island cluster may flow into the right or the left sites and the newly produced states are described as Ψ_R and Ψ_L. The difference of population of these two states are statistically estimated by the Boltzmann distribution as

$$\omega(\boldsymbol{E}) = \frac{e^{e\boldsymbol{r}_0\cdot\boldsymbol{E}/kT} - e^{-e\boldsymbol{r}_0\cdot\boldsymbol{E}/kT}}{e^{e\boldsymbol{r}_0\cdot\boldsymbol{E}/kT} + e^{-e\boldsymbol{r}_0\cdot\boldsymbol{E}/kT}} = \frac{e\boldsymbol{r}_0\cdot\boldsymbol{E}}{kT} \tag{18}$$

where $\boldsymbol{r}_0$ is the distance between the center of two TCNQs. Here we have assumed that the positive charges on the cation site are fixed.

The crystalline structure analysis on TTF(TCNQ) showed that the lattice spacing is uniform for one unit translation, and it implies that electrons and holes are delocalized over more than several lattice sites but not fixed at particular sites without any activation energy at high temperature phase.

The probability of electron transfer between the island and alternant sites may be evaluated by the Fermi golden rule assuming that the transition is isoenergetic. Namely the transition rates are given by

$$W_{\mathrm{R}} = \frac{2\pi}{\hbar}|\langle\phi_{\mathrm{R}}|H|\phi_0\rangle|^2\rho_{\mathrm{R}}(\varepsilon, \boldsymbol{E}) \tag{19}$$

or

$$W_{\mathrm{L}} = \frac{2\pi}{\hbar}|\langle\phi_{\mathrm{L}}|H|\phi_0\rangle|^2\rho_{\mathrm{L}}(\varepsilon, \boldsymbol{E})$$

where $\rho(\varepsilon, \boldsymbol{E})$ is the state density under the field, which is approximated by the reciprocal of the band width $2t$ multiplied by the field factor, and $\rho_{\mathrm{R}}(\varepsilon, \boldsymbol{E})$ and $\rho_{\mathrm{L}}(\varepsilon, \boldsymbol{E})$ are differently populated when the field is applied, say into the right direction, as

$$\rho_{\mathrm{R}}(\varepsilon, \boldsymbol{E}) - \rho_{\mathrm{L}}(\varepsilon, \boldsymbol{E}) = \omega(\boldsymbol{E})/2t \tag{20}$$

The fluctuation time of electron, τ_{R} and τ_{L}, are related to these probabilities as $\tau_{\mathrm{R}}=1/W_{\mathrm{R}}$ and $\tau_{\mathrm{L}}=1/W_{\mathrm{L}}$. The flow of electron along the applied field will be given by

$$\begin{aligned} \boldsymbol{J}_{\mathrm{R}} &= er_0\left(\frac{1}{\tau_{\mathrm{R}}}-\frac{1}{\tau_{\mathrm{L}}}\right) \\ &= \frac{\pi}{\hbar}t\cdot er_0\cdot\omega(\boldsymbol{E}) \end{aligned} \tag{21}$$

where t is the transfer integral evaluated in the previous section. The conductivity σ per unit length is given by $\boldsymbol{J}/\boldsymbol{E}$ multiplied by n, the number of mobile electron along the chain in an unit volume, as

$$\sigma = \frac{\pi}{\hbar}t\cdot(er_0)^2\frac{n}{kT} \tag{22}$$

and the numerical value is easily evaluated as 2950 Ω^{-1}cm^{-1} for the case of equal mixing of the island and the alternant configurations with an electron transfer of 0.585 from TTF to TCNQ, and it is 1231 Ω^{-1} cm^{-1} for an electron transfer of 0.50 at 300 K. The observed values are in the range of 500—1000 Ω^{-1} cm^{-1} according to Cohen, Coleman, Garito and Heeger.32) The temperature dependence of the conductivity is T^{-1} by Eq. 22, however, Groff, Suna and Merrified34) reported $T^{-2.3}$ behaviour in this crystal. If the number of electron transfer or back transfer from TTF to TCNQ has T^{-1} dependence, then n in Eq. 22 may also shows T^{-1} dependence, and the observed tendency may be qualitatively explained.

Here we have localized the cation charges on particular sites, but it may fluctuate also, and this fluctuation will be essential for good conductivity as mentioned before. If we suppose that a similar electron configuration exists for the cation column and count the contribution of both chain independently, the value of conductivity may be approximately doubled and the expected maximum value at 58 K may be 3×10^4 Ω^{-1}cm^{-1}. The ideally coherent motion of electron in both chains may be involved in the giant conduction31) particularly observed in this crystal. As another example, a recent measurement of the highest organic conductivity at room temperature by Bloch, Cowan, Bechgaard, Pyle, Banks and Poehler74) on (HMTSF) (TCNQ) showed the value as large as 1391 to 2178 Ω^{-1} cm^{-1}, which are nearly the same magnitude with the maximum value of the above mentioned mechanism.

For other alternant type crystals like NMP and Q(TCNQ), the mixing of the island configuration is smaller than for TTF(TCNQ), and a similar calculation is carried out by assuming that the electron transfer occurs at the island site and its population is determined from the spectral analysis. The results are as follows; NMP(TCNQ), $\sigma_{\mathrm{calcd}}=220$ Ω^{-1} cm^{-1}, $\sigma_{\mathrm{obsd}}=180$2)—200$^{47)}$ Ω^{-1} cm^{-1}; Q(TCNQ), $\sigma_{\mathrm{calcd}}=410$ Ω^{-1} cm^{-1}, $\sigma_{\mathrm{obsd}}=100$67) — 70$^{71)}$ Ω^{-1} cm^{-1}. These results are in fairly good agreement to each other.

As regard to the giant conductivity of TTF(TCNQ) at low temperature, Anderson, Lee, and Saitoh75) have presented a view that the activation energy may be the coupling energy of Josephson junction. Interestingly, these authors and Lee, Rice, and Anderson 76,77) thought that the Peierls transition occurs already at room temperature. Our viewpoint on this system is that the longer period than the short period of normal lattice is already mixed in at room temperature, and an apparent lattice constant may represent the averaged period, hence our view may involve the same content as Anderson *et al.*75—77) With TTF(TCNQ) the diffuse X-ray lines were observed by Denoyer, Comes, Garito, and Heeger78) and Kagoshima, Anzai, Kajinuma, and Ishiguro79) even at room temperature which indicated that the longer period than the normal lattice might be mixed. Although these authors explained it by the Kohn anomaly in the one-dimensional metallic lattice, but we may explain it by a partial mixing of the island type structure, which may have nearly triple lattice period.

Next we may try to estimate the polarizability and hence the dielectric constant in the static field for the mixed alternant and island type crystals. The polarizability α and the dielectric constant ε of the TCNQ chain may be given by

$$\begin{aligned} \alpha &= \bar{m}(\boldsymbol{E})/\boldsymbol{E} = \langle\phi_{\mathrm{R}}|er|\phi_{\mathrm{R}}\rangle\omega(\boldsymbol{E})/\boldsymbol{E} \\ &\simeq b^2\frac{(er_0)^2}{kT} \end{aligned}$$

and

$$\varepsilon = 1 + 4\pi N\alpha \tag{23}$$

where Nb^2 is the number of active site in an unit volume of the crystal. The calculated results are $\varepsilon=3400$ for TTF(TCNQ) and $\varepsilon=330$ for NMP(TCNQ) at 4.2 K. The observed values are $\varepsilon=(3.2\pm0.7)\times10^3$ for TTF-(TCNQ)80) and $\varepsilon=350\pm50$81) for NMP(TCNQ). The agreement between the observed and calculated results is quite satisfactory in spite of our simple model used for the calculation. Although our calculation on TTF(TCNQ) is based on the structure determined at room temperature, but we believe that the basic electronic structure is the same even at 4.2 K. In the low temperature phase below 54 K, the correlation of electronic motion may be lost within and between chains, presumably because a 3D regularity inhibits a labile electron motion as in other island type crystals.

Finally we must comment on the design of good conducting organic molecules. First of all good conducting TCNQ complexes which we have studied have an alternant electron configuration as the basic unit and the admixture of an island type configuration increases the conductivity significantly. In this respect a perfectly charged chain is not suitable, and a column with some vacancies will be essential.

A good overlap between TCNQ molecules will be, undoubtedly, very important in the intermolecular interaction, but the size of the transfer integral is limited as large as 0.15 eV between $TCNQ^0$ and $TCNQ^-$. Hence a small U' value for the alternant system may be significant to increase the mixing of the island type, and it may drop even to nearly zero value for some particular crystals by the balance of Coulomb forces within and between columns. The good overlap and the formation of the one-dimensional column of the donor (cation) group is also a necessary condition, because our experience shows that all good conducting crystals have both TCNQ and cation columns. It will imply that a nice balance of charges and a coherent motion of electrons and holes will be possible or facilitated by the interaction between two columns through the variable electron transfer mechanism and a correlation of Coulombic interaction. Anyway the fluctuation of the charges in the chain and the fractional charge transfer between the donor and the acceptor columns are most important for the good conductivity. It necessarily imposes a critical condition for the donor and the acceptor molecules to have a peculiar character that their radicals must be stable enough to form a complex chain with their parent molecules. It means that excess charges must be shared between several molecules, and this condition is actually satisfied in TCNQ complexes as well as TTF complexes.[81]

In concluding this paper the importance of the optical studies of these complexes must be emphasized, particularly in the infrared region, because it will give fundamental information of the electronic structure of these crystals. Although our treatment is concentrated on the molecular approach, but the physical parameters found in this study will be useful even for the band theoretical investigations.

The authors are grateful to Professors Makoto Okawara and Dwaine O. Cowan for the kind gifts of TTF(TCNQ) crystals, and to Dr. Jerry B. Torrance for kind information and comment. They also thank to Professor Yoshihiko Saito for many crystallograpflic information, and to Drs. Motomichi Inoue and Hitosi Sumi for helpful discussions. One of the authors (J. T.) thanks to Professors Takehiko Shimanouchi and Takeo Yamamoto of the University of Tokyo for the use of the Tool-IR system of the Computation Center of the University of Tokyo.

References

1) Z. Soos, *Ann. Rev. Phys. Chem.*, **25**, 121 (1974).

2) I. F. Shchegolev, *Phys. Status Solidi A*, **12**, 4 (1972).

3) F. H. Herbstein, *Perspect. Struct. Chem.*, **4**, 166, ed. by J. D. Dunitz and J. A. Ibers, John Wiley (1971).

4) A. J. Heeger and A. F. Garito, "Low Dimensional Cooperative Phenomena," ed. by H. J. Keller, Plenum Press, New York (1975), p. 89.

5) J. Kommandeur, "Low Dimensional Cooperative Phenomena," ed. by H. J. Keller, Plenum Press, New York (1975), p. 65; J. G. Vegter, J. Kommandeur, and P. A Fedders, *Phys. Rev.* **B7**, 2929 (1973); J. G. Veger, P. I. Kuindersma, and J. Kommandeur, "Conduction in low-mobility materials," Taylor and Francis, (1971): J. G. Vegter and J. Kommandeur, *Mol. Cryst. Liq. Cryst.* **30**, 11 (1975).

6) 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).

7) L. R. Melby, *Can. J. Chem.*, **43**, 1448 (1965).

8) H. Kobayashi, F. Marumo, and Y. Saito, *Acta Crystallogr.* **B27**, 373 (1971).

9) A. W. Hanson, *Acta Crystallogr.*, **B24**, 768 (1968).

10) H. Kobayashi, *Bull. Chem. Soc. Jpn.*, **47**, 1346 (1974).

11) T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, *Acta Crystallogr.* **B30**, 763 (1974).

12) R. H. Blessing and P. Coppens, *Solid State Comm.*, **15**, 215 (1974).

13) P. Coppens, *Phys. Rev. Lett.*, **35**, 98 (1975).

14) W.D. Grobman, R. A. Pollak, E. E. Eastman, E. T. Mass, Jr., and B. A. Scott, *Phys. Rev. Lett.*, **32**, 534 (1974).

15) W. T. Wozniak, G. Depasquali, M. V. Klein, R. L. Sweany, and T. L. Brown, *Chem. Phys. Lett.*, **33**, 33 (1975).

16) C. J. Fritchie, Jr. and P. Arthur Jr., *Acta Crystallogr.*, **21**, 139 (1966).

17) H. Kobayashi, Y. Ohashi, F. Marumo, and Y. Saito, *Acta Crystallogr.*, **B26**, 459 (1970).

18) M. Konno and Y. Saito, *Acta Crystallogr.*, **B30**, 1294 (1974); *ibid.*, **B31**, 2007 (1975).

19) M. Konno and Y. Saito, *Acta Crystallor.*, to be published.

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

21) D.A. Lowitz, *J. Chem. Phys.*, **46**, 4698 (1967).

22) Y. Iida, *Bull. Chem. Soc. Jpn.*, **42**, 71, 673 (1969).

23) J. Hubbard, *Proc. R. Soc., Ser. A*, **276**, 238 (1963); **281**, 401 (1964); **285**, 542 (1965).

24) A. J. Berlinsky, J. F. Coleman, and L. Weiler, *Solid State Commun.* **15**, 795 (1974).

25) E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.*, **127**, 1618 (1962).

26) S. Hiroma, H. Kuroda, and H. Akamatu, *Bull. Chem. Soc. Jpn.*, **44**, 9 (1971).

27) O. H. LeBlanc, Jr., *J. Chem. Phys.* **42**, 4307 (1965).

28) A. Hoekstra, T. Spoelder, and A. Vos, *Acta Crystallogr.*, **B28**, 14 (1972).

29) N. Sakai, I. Shirotani, and S. Minomura, *Bull. Chem. Soc. Jpn.*, **45**, 3314 (1972).

30) Y. Ohashi and T. Sakata, *Bull. Chem. Soc. Jpn.*, **46**, 3330 (1973).

31) L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.* **12**, 1125 (1973).

32) M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, *Phys. Rev.*, **B10**, 1298 (1974).

33) J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 348 (1973).

34) R. P. Groff, A. Suna, and R. E. Merrifield, *Phys. Rev. Lett.*, **33**, 418 (1974).

35) P. M. Grant, R. L. Greene, G. C. Wrighton, and G. Castro, *Phys. Rev. Lett.*, **31**, 1311 (1973).

36) C. S. Jacobsen, D. B. Tanner, A. F. Garito, and A. J. Heeger, *Phys. Rev. Lett.*, **33**, 1559 (1974); D. B. Tanner, C.S. Jacobsen, A. F. Garito, and A. J. Heeger, *Phys. Rev.*, **B13**, 3381 (1976).

37) J. B. Torrance, B. A. Scott, and F. B. Kaufman, *Solid State Commun.* **17**, 1369 (1975).

38) M. Tanaka, J. Tanaka, C. Tanaka, and H. Anzai, unpublished results.

39) F. Wudl, G. M. Smith, and E. G. Hutnagel, *Chem. Commun.* **1970**, 1453.

40) J. B. Torrance, private communication.

41) A. A. Bright, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **13**, 943 (1973); *Phys. Rev.*, **B10**, 1328 (1974); D. B. Tanner, C. S. Jacobsen A. F. Garito, and A. J. Heeger, *Phys. Rev. Lett.*, **32**, 1301 (1974).

42) H. Hinkelmann and H. G. Reik, *Solid State Commun.*, **16**, 567 (1975).

43) Y. Ueno, Y. Masuyama, and M. Okawara, *Chem. Lett.* **1975**, 603; Y. Ueno and M. Okawara, *ibid.*, **1975**, 1135.

44) L. B. Coleman, S. K. Khanna, A. F. Garito, A. J. Heeger, and B. Morosin, *Phys. Lett.*, **42A**, 15 (1972); the structure of a monoclinic form was briefly reported by B. Morosin, *Phys. Lett.*, **53A**, 455 (1975).

45) C. J. Fritchie, Jr., *Acta Crystallogr.*, **20**, 892 (1966).

46) H. Kobayashi, *Bull. Chem. Soc. Jpn.*, **48**, 1373 (1975).

47) A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, *Phys. Rev.*, **B5**, 952 (1972).

48) T. Sakata and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **42**, 1497 (1969).

49) B. H. Schechtman, S. F. Lin, and W. E. Spicer, *Phys. Rev. Lett.*, **34**, 667 (1975).

50) T. Sundaresan and S.C. Wallwork, *Acta Crystallogr.*, **B28**, 491 (1972).

51) A. T. McPhail, G. M. Semeniuk, and D.B. Chesnut, *J. Chem. Soc., A*, **1971**, 2174; M. Konno and Y. Saito, *Acta Crystallogr.*, **B29**, 2815 (1973).

52) J. Tanaka, M. Inoue, M. Mizuno, and K. Horai, *Bull. Chem. Soc. Jpn.*, **43**, 1998 (1970).

53) J. C. Scott, A. F. Garito, and A. J. Heeger, *Phys. Rev.*, **B10**, 3131 (1974).

54) Y. Tomkiwicz, B. A. Scott, L. J. Tao, and R. S. Title, *Phys. Rev. Lett.*, **32**, 1363 (1974); J. E. Gulley and J. F. Weiher, *ibid.*, **34**, 1061 (1975).

55) J. C. Bonner and M. E. Fisher, *Phys. Rev.*, **135**, A640 (1964).

56) T. Hibma, P. Dupuis, and J. Kommandeur, *Chem. Phys. Lett.*, **15**, 17 (1972).

57) R. M. Vlasova, I. A. Smirnov, L. S. Sochava, and A. I. Skerle, *Fiz. Tverd. Tela*, **10**, 2990 (1968).

58) J. C. Bailey and D. B. Chesnut, *J. Chem. Phys.*, **51**, 5118 (1969).

59) R. G. Kepler, *J. Chem. Phys.*, **39**, 3528 (1963).

60) D. B. Chesnut and P. Arthur, Jr., *J. Chem. Phys.*, **36**, 2969 (1962).

61) D. B. Chesnut and W. D. Phillips, *J. Chem. Phys.*, **35**, 1002 (1961).

62) L. Shields, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1372 (1974). A value of 0.072 eV will be reported by G. J. Ashwell, D. D. Eley, I. Diaconu, M. R. Willis, and J. Woodward; a private communication of M. R. Willis.

63) T. Sundaresan and S. C. Wallwork, *Acta Crystallogr.*, **B28**, 3507 (1972).

64) H. Kobayashi, T. Danno, and Y. Saito, *Acta Crystallogr.*, **B29**, 2693 (1973).

65) D. Chasseau, J. Ganltier, C. Hauw, and M. Schvoerer, *C. R. Acad. Sci., Paris, Ser. C*, **275**, 1491 (1972).

66) T. Sundaresan and S. C. Wallwork, *Acta Crystallogr.*, **B28**, 2474 (1972).

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

68) A. A. Ovchinikov, *Sov. Phys. JETP*, **30**, 1160 (1970).

69) N. F. Mott, *Adv. Phys.*, **13**, 325 (1964).

70) Y. Suezaki, *J. Phys. Soc. Jpn.*, **34**, 89 (1973).

71) L. I. Buravov, D. N. Fedutin, and I. F. Shchegolev, *Sov. Phys. JETP*, **32**, 612 (1971).

72) R. C. Wheland and J. L. Gillson, to be published.

73) A. N. Bloch, D. O. Cowan, and T. O. Pohler, "Energy and Charge Transfer in Organic Semiconductor," ed. by K. Masuda and M. Silver, Plenum Press (1974).

74) A. N. Bloch, D. O. Cowan, K. Bechgaard, R. E. Ryle, R. H. Banks, and T. O. Poehler, *Phys Rev. Lett*, **34**, 1561 (1975).

75) P. W. Anderson, P. A. Lee, and M. Saitoh, *Solid State Commun.*, **13**, 595 (1973).

76) P. A. Lee, T. M. Rice, and P. W. Anderson, *Phys. Rev. Lett.*, **31**, 462 (1973).

77) P. A. Lee, T. M. Rice, and P. W. Anderson, *Solid State Commun.*, **14**, 703 (1974).

78) F. Denoyer, F. Comes, A. F. Garito, and A. J. Heeger, *Phys. Rev. Lett.*, **35**, 445 (1975).

79) S. Kagoshima, H. Anzai, K. Kajinuma, and T. Ishiguro, *J. Phys. Soc. Jpn.*, **39**, 1143 (1975).

80) S. K. Khanna, A. F. Garito, A. J. Heeger, and R. C. Jaklevic, *Solid State Commun.*, **16**, 667 (1975); S. K. Khanna, E. Ehrenfreund, A. F. Garito, and A. J. Heeger, *Phys. Rev.*, **B10**, 2205 (1974).

81) F. Wudl, E. E. Schafer, W. M. Walsh, Jr., L. W. Rupp, F. J. DiSalvo, J. V. Waszczak, M. L. Kaplan, and G. A. Thomas, to be published.