An X-Ray Analysis of the Orientational Disorder of *N*-Methylphenazinium-TCNQ

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The X-ray diffraction patterns of NMP-TCNQ show diffuse streaks along the c* direction. The analysis of the intensities of these streaks revealed that the orientation of NMP is one-dimensionally disordered along the c axis. The structure obtained indicates that the potential exerting on an electron moving in a column of TCNQ is not random, but can be expressed by a periodic function; this implies that NMP-TCNQ can not be regarded as a disordered one-dimensional conductor. The periodicity of the potential means that the one-dimensional energy band must be filled.

N-Methylphenazinium-7,7,8,8-tetracyanoquinodimethanide (NMP-TCNQ) is one of the highly conducting TCNQ salts. The physical properties of the salt have been intensively investigated.[1] Based on the theorem that the electronic states in any disordered one-dimensional structure are localized, Bloch, Weisman, and Varma (BWV) have explained the temperature dependence of the electrical conductivity of NMP-TCNQ.[2] Their interpretation depends on Fritchie's average structure of NMP-TCNQ[3] and the published electrical conductivity of Shchegolev *et al.*[4] NMP is located at the position of (1/2, 1/2, 1/2), whose site symmetry is $\bar{1}(C_i)$, taking either of the two possible orientations as equally probable (Fig. 1). This disorder seems to be

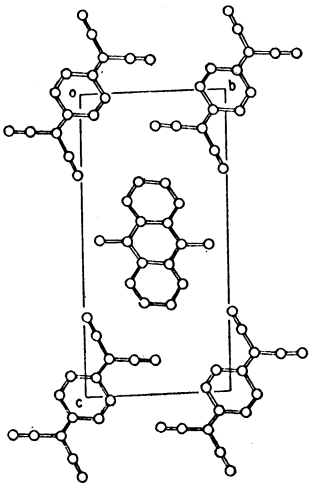

Fig. 1. The avarage structure of NMP-TCNQ.[3]

able to produce a potential which varies randomly along a TCNQ column. The low-temperature conductivity can be approximately fitted by $\ln \sigma \sim (T_0/T)^{1/2}$, derived for a disordered one-dimensional system by the application of the theories of Mott and Ambergaakar, Halperin, and Langer.[2] On the other hand, Heeger *et al.*[1,5,6] regarded NMP-TCNQ as a realization of the one-dimensional Mott-Hubbard model, with the disorder playing only a peripheral role. Their experimental study and analysis of the low-temperature conductivity of high-purity single crystals of NMP-TCNQ revealed that the plot of $\log_{10}(\sigma/\sigma_0)$ *vs.* $1/T$ shows straight-line behavior; this is not consistent with the analysis of BWV. Because of the electron-electron Coulomb repulsion, the electron localizes to from a magnetic insulator at low temperatures. The magnitude of the Hubbard gap goes smoothly to zero at *ca.* 200 K.[6] In this paper, the details of the orientational disorder will be reported in order to contribute to a better knowledge of one-dimensional conductors.

Experimental

The specimens of *N*-methylphenazinium-7,7,8,8-tetracyanoquinodimethanide(NMP-TCNQ: $C_{13}H_{11}N_2 \cdot C_{12}H_4N_4$) was kindly supplied by Ichimin Shirotani, who has paid particular

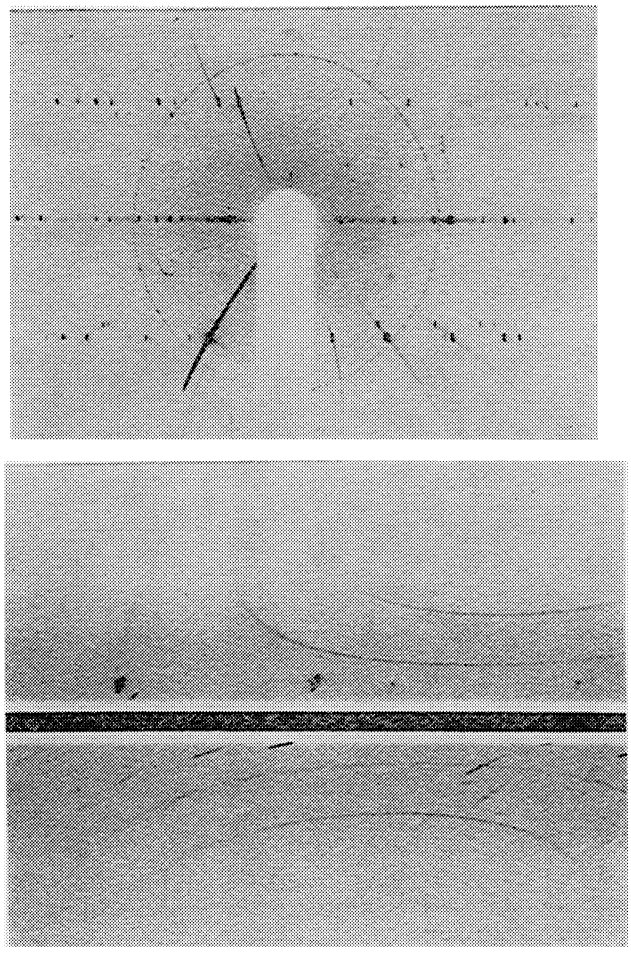

Fig. 2. (a) Oscillation photograph: weak reflections observable in the middle of the strong layer lines
(b) Weissenberg photograph (1/2, η, ζ)

attention to the purification of the samples.[7] The single crystals are black needles, with long axes parallel to the crystallographic a axis. The lattice constants has been reported to be[3]: $a=3.8682$, $b=7.7807$, $c=15.735$ Å, $\alpha=91.67$, $\beta=92.67$, $\gamma=95.38°$ (at 23 °C); space group: $P\bar{1}$. TCNQ and NMP are stacked separately along the a axis to form modadic columns.

Although oscillation and Weissenberg photographs indicated that the intensity distribution of Bragg reflections is the same as that given in Fritchie's paper,[3] a closer examination revealed that diffuse streaks occur along the c* direction in the middle of the strong layer lines around the a axis (Fig. 2). These faint X-ray scatterings were overlooked in an earlier analysis by Fritchie.[3] The streaks appear at the $(h+1/2, k, \zeta)$ position of the reciprocal space, where h and k are integers and where $(h+1/2)\boldsymbol{a}^*+k\boldsymbol{b}^*+\zeta\boldsymbol{c}^*$ is the scattering vector, $\boldsymbol{k}$. The intesities along the streaks vary slowly, and no sharp maxima were observed. Similar streaks were also observed in a Weissenberg photograph of 3/2 layer line around the a axis. All the experiments were performed at room temperature.

Analysis of the Diffuse Streaks and Discussion

The extra reflections indicate: (1) the arrangement of NMP and TCNQ is regular in each a-b layer, but each layer has no correlation to the adjacent layers, and (2) in each a-b layer, the lattice period along the a direction is twice the reported value. Thus, the Fritchie's structure must be regarded as the average structure of the one-dimensionally disordered lattice.

The probable models of the disordered structure could then be easily deduced.

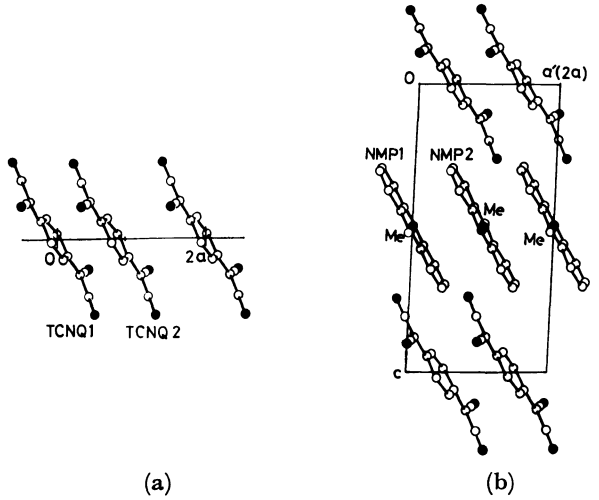

Fig. 3. The models of the molecular arrangement
(a) Model I (rejected) (b) Model II (true)

Model I: TCNQ are not stacked with an equal intermolecular spacing; rather, two different spacings appear alternately, as is found in simple salts of TCNQ[8,9] (Fig. 3a). Each TCNQ is shifted from its position in the average structure by $\varepsilon\boldsymbol{a}$ or $-\varepsilon\boldsymbol{a}$, while the orientation of NMP is disordered in the same way as in the average structure.

Model II: Two possible orientations of NMP alternate along the a axis (Fig. 2). On the other hand, the arrangement of TCNQ is the same as that given by Fritchie.

The important role of the dimeric arrangement of $TCNQ^-$ anions has been previously discussed in connection with the monomer-dimer transition of the simple salts of TCNQ[9] and a Peierls transition of one-dimensional conductors.[10,11] However, Model I can not explain the features of the X-ray diffraction patterns. Based on Model I, the intensities of the streaks are expressed as:

$$I_D(k) = \sum_{ij}\chi_{ij}(f_1-f_2)^2 \exp(i\boldsymbol{k}\boldsymbol{R}_{ij})$$

where $\boldsymbol{R}_{ij}=\boldsymbol{R}_i-\boldsymbol{R}_j$ ($\boldsymbol{R}_i$ is the lattice vector of the i-th lattice point), $\boldsymbol{k}$ is the scattering vector $(\xi\boldsymbol{a}^*+\eta\boldsymbol{b}^*+\zeta\boldsymbol{c}^*)$, χ_{ij} is the correlation function representing the mode of the disorder of the arrangement of TCNQ, and f_1 and f_2 are the scattering factors of TCNQ shifted by $\varepsilon\boldsymbol{a}$ and $-\varepsilon\boldsymbol{a}$ respectively. $I_D(\boldsymbol{k})$ is closely related to the molecular structure factor of TCNQ, because f_1-f_2 can be written as:

$$f_1-f_2 = 2\{\sum_j f_j \cos 2\pi(\xi x_j+\eta y_j+\zeta z_j)\}\sin 2\pi\xi\varepsilon$$

where f_j is the atomic scattering factor of the j-th atom and where (x_j,y_j,z_j) is the atomic coordinate. The general features of the calculated intensity curves do not resemble those of the observed curves. Especially, according to this intensity formula, a very strong streak must be observed at the reciprocal point $(1/2,0,\zeta)$; however, the intensities were, in fact, too weak to be observed. Thus, Model I was rejected.

Using Model II, the structure factors of the disordered lattice can be written as:

$$F(k) = \sum_j\{f_{TCNQ}+(n_jf_{NMP\uparrow}+(1-n_j)f_{NMP\downarrow})\}\exp(i\boldsymbol{k}\boldsymbol{R}_j)$$

where f is a molecular scattering factor; NMP↑ and NMP↓ indicate two types of the orientations of NMP, and n_j is the probability that the orientation of NMP in the j-th cell is that of NMP↑. The corresponding intensity is given by[12]:

$$I(k) = |\langle F(k)\rangle|^2 = I_B + I_D$$

where

$$I_B(k) = |\sum_j(f_{TCNQ}+f_{NMP})\exp(i\boldsymbol{k}\boldsymbol{R}_j)|^2$$

and by:

$$I_D(k) = \sum_{jj'}\chi_{jj'}(f_{NMP\uparrow}-f_{NMP\downarrow})^2\exp(i\boldsymbol{k}\boldsymbol{R}_{jj'})$$

where $f_{NMP}=(f_{NMP\uparrow}+f_{NMP\downarrow})/2$, $\langle\ \rangle$ indicates the statistical average and where the correlation function, $\chi_{jj'}$, is expressed as

$$\chi_{jj'} = \langle(n_j-\langle n\rangle)(n_{j'}-\langle n\rangle)\rangle$$

I_B represents the reflections from the lattice with the average structure, which is the same as that derived by Fritchie[3], while I_D is due to the disorder of the crystal. Besides the methyl group, NMP is centrosymmetric. By the use of the atomic parameters of the methyl carbon given by Fritchie, $(f_{NMP\uparrow}-f_{NMP\downarrow})$ may be written simply as:

$$f_{NMP\uparrow}-f_{NMP\downarrow} = 2f_C\sin 2\pi(-0.0328\xi+0.3750\eta+0.0141\zeta),$$

where f_C is the scattering factor of a carbon atom. The correlation function of the orientation of NMP between

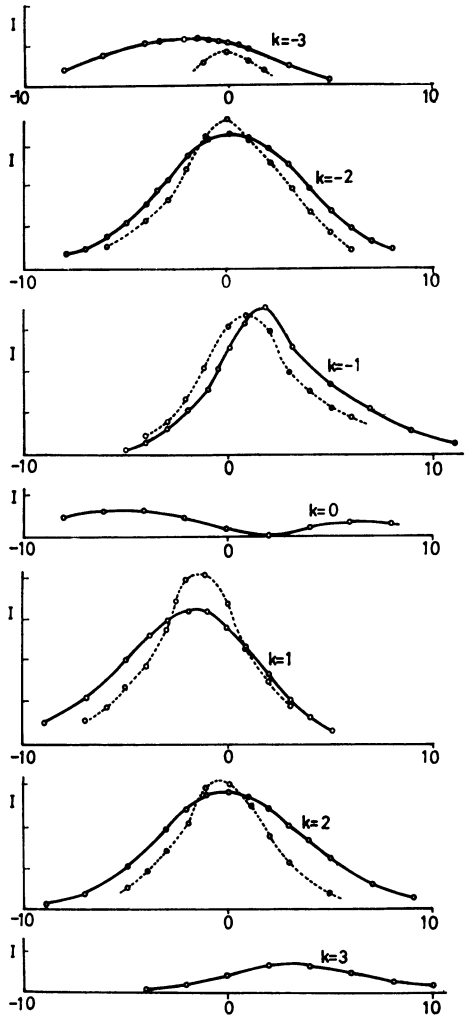

Fig. 4. The observed (broken lines) and calculated (solid lines) intensities of the streaks. The streaks were not observed ($I_{obs}=0$) for $k=0$ and 3. The intensities are plotted as ordinate and the values of ζ as abscissa. Scattering vector $\boldsymbol{k}$ is $\boldsymbol{a}^*/2+k\boldsymbol{b}^*+\zeta\boldsymbol{c}^*$.

i-th and j-th sites ($\boldsymbol{R}_{ij}=n_1\boldsymbol{a}+n_2\boldsymbol{b}+n_3\boldsymbol{c}$) is

$$\chi_{ij}=\begin{cases} 1/4 \cdots n_1=2m \text{ and } n_3=0 \\ -1/4 \cdots n_1=2m+1 \text{ and } n_3=0 \\ 0 \cdots n_3 \neq 0 \end{cases}$$

Because of the orientational disorder, the observed temperature factor of the methyl carbon is very large[3]; it was, therefore, replaced by that of the nitrogen atom of NMP in the calculation of I_D. The observed and calculated intensities of the streaks of the 1/2-layer line ($\xi=1/2$) are compared in Fig. 4. The scale of the observed intensities was adjusted so as to give the best fit to the calculated ones. The comparison was not attempted for the streaks of the 3/2-layer line because of the weakness of the intensities. Considering the roughness of the estimation of the temperature factor, the agreement is satisfactory. Therefore, we may conclude that Model II represents the real structure of NMP-TCNQ.

The molecular arrangement of NMP-TCNQ thus obtained is shown in Figs. 3b and 5. Two orientations of NMP alternate along the a axis, while one fixed orientation is repeated along the b direction. The

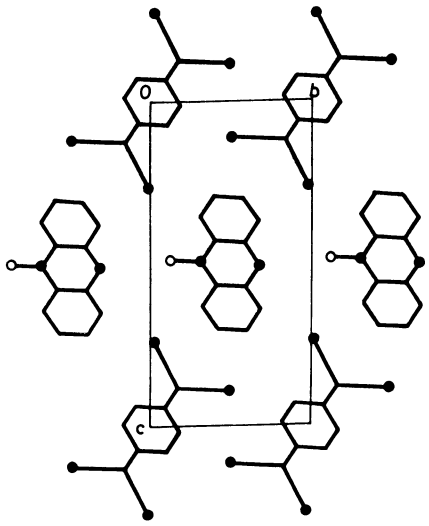

Fig. 5. A regular sequence of NMP along the b axis. This and the other arrangements of NMP with opposite orientations alternate along the a axis to form a regular *a–b* layer. Such regular layers of NMP are randomly correlated with each other along the c axis.

correlation of the orientation dose not exist between NMP, which belong to different *a–b* layers. The unusually short contact of 2.01 Å between two neighbouring methyl carbons which occur randomly in the average structure dose not exist in the real structure. The two-dimensionally ordered molecular arrangement in each *a–b* layer seems to be natural in view of the dipole-dipole interaction between NMP(Fig. 6). There is no direct intermolecular contact of NMP along the c direction. Thus, this type of one-dimensional disorder is very likely to occur in this crystal.

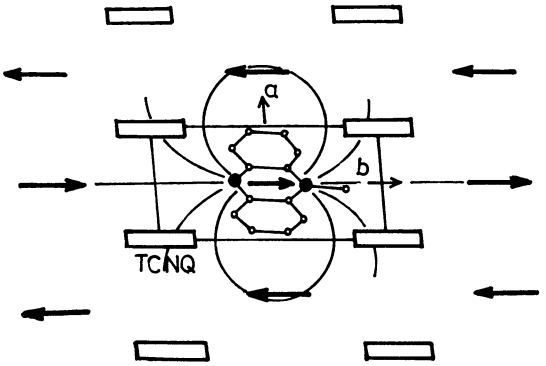

Fig. 6. Schematic drawing of the two-dimensionally ordered arrangement of NMP and TCNQ and an electric field due to a dipole moment of an NMP.

The localized model of BWV has been criticized by Heeger *et al.*,[5,6] Kurkijarvi,[13] and Suezaki.[14] Suezaki suggested the possibility that the randomness in NMP-TCNQ is insufficient to adopt the localized model, since the possible orientations of NMP are restricted in two directions, as has been shown in an earlier crystal structure analysis.[3] From the structural viewpoint, we can show evidence that the localized model of BWV is not suited for the interpretation of the electrical properties of NMP-TCNQ. Let us consider an electric potential being exerted on an electron moving along

a column of TCNQ. Within a simple noninteracting-electron approximation, the Hamiltonian can be written as

$$H(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \sum_j V_j(x)$$

where V_j is the potential due to the ions in the j-th layer and where x is the coordinate of the electron in this column. Since all ions in each a-b layer are arranged regularly with a period of $2a$(7.736 Å), $V_j(x)$ must be a periodic function:

$$V_j(x+2a) = V_j(x).$$

Therefore, the total potential, $V(x)(=\sum V_j(x))$, is also periodic along the TCNQ column parallel to the a axis. Thus, the localized model of BWV which is based on the assumption of the random potential along the column of TCNQ can not be adopted in the interpretation of the electrical properties of NMP-TCNQ. In addition, based on this periodicity of the potential function $V(x)$, it is easy to see that there are some difficulties in the application of the one-dimensional half-filled-band Hubbard model proposed by Heeger *et al.*[1,6] Because the periodic unit is $2a$, the Bloch function $\psi(x)$ can be given as:

$$\psi(x) = \exp(ikx)u_k(x)$$
$$-\pi/2a < k \leqq \pi/2a$$

The corresponding energy band is shown schematically in Fig. 7a. There are two excess electrons in each periodic unit, so the band must be filled. Therefore, NMP-TCNQ must be semiconductive, even if the electron-electron Coulomb repulsion is small (the electron-electron Coulomb repulsion produces a Hubbard gap in a half-filled-band Hubbard model (Fig. 7b)[15]). This conclusion is qualitatively consistent with the observed low-temperature conductivities of this salt.[1]

The orientational disorder of cations has also been found in the crystals of ARD-$TCNQ_2$[11] and Q-$TCNQ_2$[16], which are also highly conducting salts. However, no X-ray diffuse streaks have been observed. The modes of the arrangement of cations in these crystals are similar to each other, but they do not resemble that of NMP-TCNQ. According to BWV, the electronic properties of these salts can also be interpreted by means of the localized model. In the crystals of ARD-$TCNQ_2$ and Q-$TCNQ_2$, the cations are stacked to form monadic columns of ARD and Q respectively. As is shown in Fig. 8, however, these columns of cations are surrounded by six TCNQ columns and have no direct contact between them. Therefore, the features of the orientational disorder in these complex salts are probably different from those in the simple NMP-TCNQ salt described above.

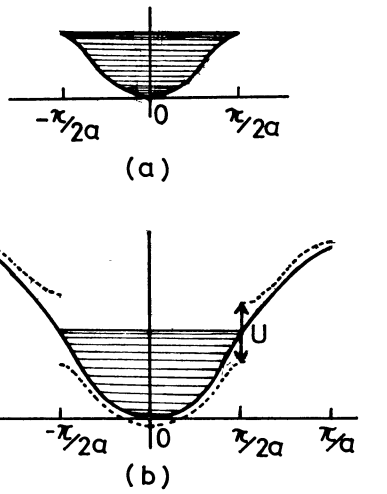

Fig. 7. Schematic drawing of the band structure of NMP-TCNQ.
(a) A filled band of one dimensionally disordered structure of NMP-TCMQ.
(b) A half-filled band of the average structure of NMP-TCNQ. Broken lines indicate the band structure in the presence of the electronic correlation and U is the magnitude of a Hubbard gap.

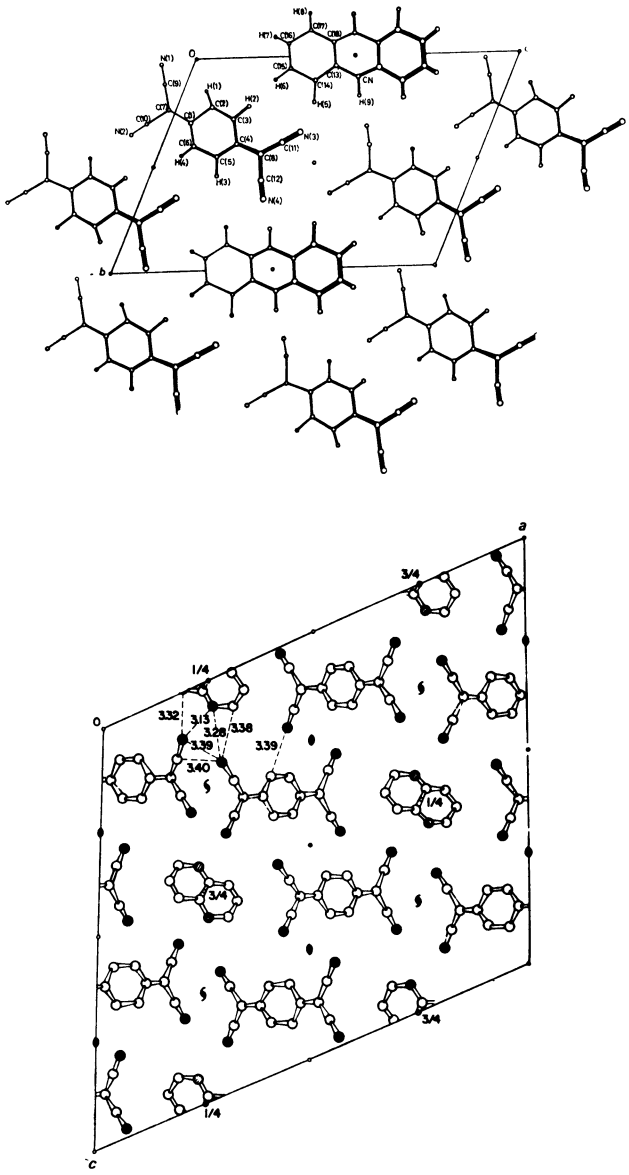

Fig. 8. The structures of ARD-$TCNQ_2$ and Q-$TCNQ_2$.
(a) ARD-$TCNQ_2$[10] (b) Q-$TCNQ_2$[15]

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