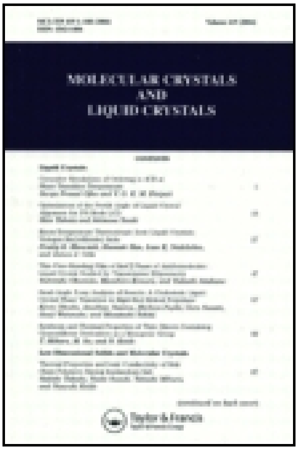

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Low-Temperature and High-Pressure Reflectance Spectra of Benzidine-Tcnq Charge-Transfer Complex

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LOW-TEMPERATURE AND HIGH-PRESSURE REFLECTANCE SPECTRA OF BENZIDINE-TCNQ CHARGE-TRANSFER COMPLEX

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Abstract Reflectance spectra of solvent-free and dichloromethane-containing single crystals of the charge-transfer complexes between benzidine and TCNQ were measured at 30 K and at 56.7 Kbar. The degree of charge transfer was estimated by their oscillator strengths of the first CT band to be 0.28 at room temperature and 0.43 at 30 K for solvent-free modification, and ~0.35 at room temperature for dichloromethane-containing modification.

INTRODUCTION

For a solid molecular complex of a mixed donor-acceptor stack, there is a borderline value of the difference between the ionization potential of the donor and the electron affinity of the acceptor, above which a charge-transfer complex of essentially neutral ground state is formed and below which an ionic complex formed. There are several molecular complexes in which the difference between the ionization potential of the donor and the electron affinity of the acceptor is just on the abovementioned borderline. The molecular complex between tetrathiafulvalene (TTF) and chloranil (CA) is one typical example of such a case, and is known to exhibit a neutral-ionic phase transition on lowering the temperature.[1,2]

The system which involves benzidine (BD) as electron donor and 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) as electron acceptor is also an example of a borderline case. Previously, we found that there are a solvent-free modification and solvent-containing modifications, all of which have essentially neutral ground states at room temperature.[3] In the present paper, we report the low-temperature reflectance spectra measured on single crystals of the solvent-free and dichloromethane-containing modifications of BD-TCNQ, and discuss the degree of charge transfer obtained from the analysis of the observed spectra. We will also present the preliminary results of the reflectance spectrum of BD-TCNQ solvent-free crystal at high pressures.

EXPERIMENTAL

The polarized reflectance spectrum was measured on a small single crystal of BD-TCNQ by use of a microspectrophotometer combined with a cryostat to keep the sample crystal at low temperature. The sample crystal is mounted on a goniometer head which is fixed on the cold head of a cryogenic refrigerator. The lowest temperature of the sample crystal attainable with this system was 30 K. Details of the apparatus and the method of analysis of reflectance data have been described elsewhere.[3,4] The high pressure reflectance spectrum of a single crystal was measured by using a diamond anvil cell. The 1:1 mixture of isopentane and n-pentane was used as a pressure medium. The applied pressure was determined by measuring the shift of the R_1 fluorescence line of ruby crystals. Single crystals of the solvent-free modification were grown by slow crystallization from a hot saturated chloroform solution containing appropriate amounts of BD and TCNQ. The dichloromethane-containing modification was prepared from a dichloromethane solution by the same method.

RESULTS AND DISCUSSION

Figure 1 shows the room-temperature and 30 K reflectance spectra measured on the (010) face of BD-TCNQ solvent-free crystal for light polarizations parallel and perpendicular to the *c* axis. In the crystal, BD and TCNQ are alternately stacked along the *c* axis as shown in Fig. 1.[5] The reflectance dispersions at 6 × 10^3 and 20 × 10^3 cm^{-1} are completely polarized parallel and perpendicular to the *c* axis, respectively. These dispersions have been assigned to the first and second CT transitions which are associated with electron transfer from the highest and second-highest occupied molecular orbitals of BD to the lowest unoccupied molecular orbital of TCNQ, respectively.[3] Note that, in

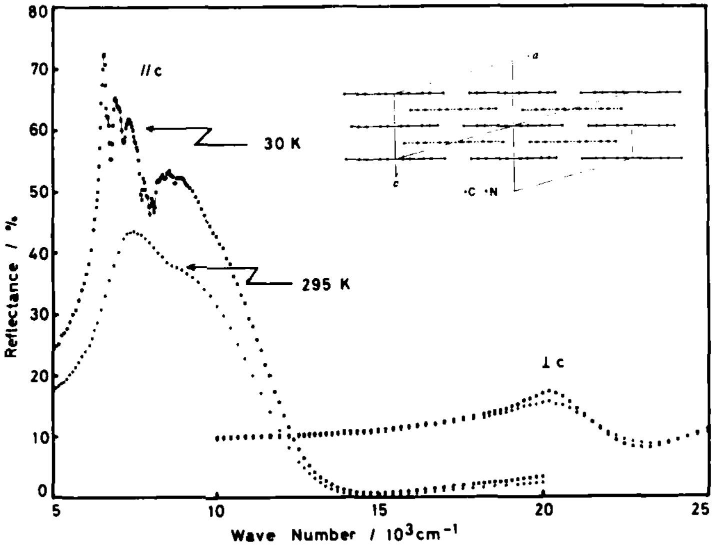

FIGURE 1 Reflectance spectrum of the BD-TCNQ solvent-free modification.

the region of the first CT transition, reflectance is significantly enhanced and a series of sharp structures appears as the crystal is cooled to 30 K, while the dispersion due to the second CT transition remains broad and structureless. We analyzed the vibrational structure of the first CT band by using the electron molecular vibration coupling constants of TCNQ reported by M. J. Rice et al.,[6] and concluded that the prominent vibrational structure arises from the intramolecular vibrations of TCNQ.[7]

The total oscillator strength of the first CT band of the BD-TCNQ crystal was calculated to be 0.61 from the reflectance data at room temperature and 0.94 from those at 30 K. A similar enhancement of the oscillator strength of CT transition on lowering the temperature has been observed also for other charge-transfer complexes.[8] This phenomenon is probably partly due to a decrease of the spacing between donor and acceptor accompanying lattice contraction and partly due to suppression of thermal vibration at low temperature, both of which may result in an increase of the overlap integral between donor and acceptor. We estimated the transfer integral of nearest-neighbor donor-acceptor pair and the degree of charge transfer using the above-mentioned values of the oscillator strength. The transfer integral, t, can be calculated by use of the relation,[9]

$$t/E_{CT} \simeq -r/(\sqrt{2}\, R_{DA}), \qquad when\ t^2/E_{CT}^2 \ll 1$$

where E_{CT} is the excitation energy of the CT transition, r, the transition dipole length of the CT transition obtained from the oscillator strength, and R_{DA}, the distance between donor and acceptor. The degree of charge transfer, δ, is given by $\delta \simeq 2t^2/E_{CT}^2$. From the oscillator strength derived from the room-temperature reflectance spectrum, the transfer integral is estimated to be 0.3 eV and the degree of charge transfer to be 0.28. We estimated the degree of charge transfer at room temperature to be 0.25 from the frequency shift of the CN stretching vibration with the aid of the method proposed by Chappell et al..[10] We used the following complexes as the standards: TCNQ (δ=0.0), quinolinium-$(TCNQ)_2$ (δ=0.5), and K-TCNQ (δ=1.0). We have carried out molecular orbital calculations by the SCF MO CI method within the framework of the π-electron approximation, treating a BD-TCNQ pair as a supermolecule.[11] This calculation gave 0.35 for the degree of charge transfer in the ground state. All these values of the degree of CT show fairly good agreement with each other. From the oscillator strength of the first CT band at 30 K, the transfer integral is estimated to be 0.38 eV and the degree of CT to be 0.43, indicating a significant increase of charge transfer.

We observed that the lowering of the temperature induced a remarkable enhancement of oscillator strength and a slight red shift for the first CT band. We examined the effect of pressure, which causes a larger lattice contraction in comparison with the lowering of temperature. Although we could not obtain reliable results as regards the absolute value of reflectance, a systematic change was found to take place in the first CT band on increasing the pressure, as shown in Fig. 2. The first CT band gradually shifts to low wavenumber, and a shoulder grows up around 10×10^3 cm^{-1} on elevating the pressure. The shift is quite large in comparison with the 30 K spectrum. The shape of the dispersion curve at 56.7 Kbar looks like the metallic reflection, which is observed in the cyanine dyes with a very strong electronic transition. This pressure dependence of the first CT band indicates that the increase of oscillator strength caused by the application of the pressure of 56.7 Kbar is larger than that caused by lowring the temperature to 30 K. However, BD-TCNQ complex is likely to remain neutral under 56.7 Kbar, because the $\perp c$ spectrum showed only a very slight change.

Figure 3 shows the reflectance spectrum measured on the

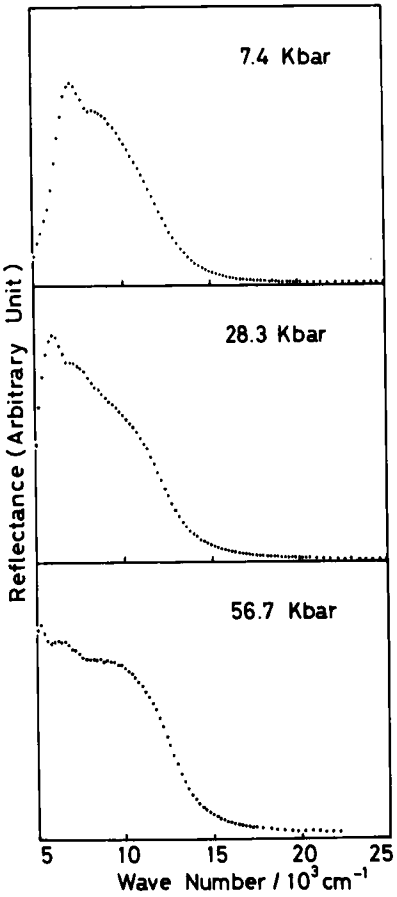

FIGURE 2 Pressure dependence of the $/\!/ c$ spectrum of the BD-TCNQ solvent-free modification.

(010) crystal face of the dichloromethane-containing modification. This crystal has a mixed stacked column of BD and TCNQ as shown in Fig. 3,[12] which is almost the same as that of solvent-free modification. The neighboring columns are connected by hydrogen bond between the amino groups of BD and the cyano groups of TCNQ. This hydrogen bond stabilizes the channel structure parallel to the column, the dichloromethane molecules being located in the channels. The distance between BD and TCNQ is shorter by 0.02 Å than that of the solvent-free modification. The *// c* spectrum measured at room temperature is almost the same as that of the solvent-free modification except that the dispersion is shifted by about 2,500 cm^{-1} to the low-wavenumber side and the reflectance is higher. Since the oscillator strength obtained by the curve fitting analysis was nearly the same

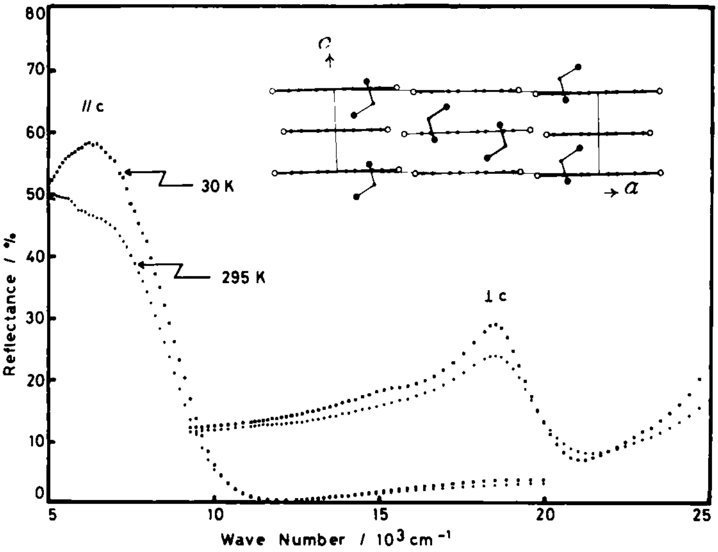

FIGURE 3 Reflectance spectrum of the BD-TCNQ dichloromethane-containing modification.

as that of the solvent-free modification and the excitation energy, E_{CT}, is smaller than that of the solvent-free modification, the degree of charge transfer is estimated to be about 0.35, which is larger than that of the solvent-free modification. This is in accord with the observation that a part of BD-TCNQ pairs is easily ionized by the mechanical grinding.[13] Not only the short distance between BD and TCNQ but also the hydrogen bond seems to play an important role in the increase of the degree of charge transfer, since BD is a proton donor and TCNQ is a proton acceptor. The 30 K reflectance spectrum is remarkably different from the corresponding spectrum of the solvent-free modification. The first CT band is structureless even at low temperature, and shifts to the high-wavenumber side at 30 K. Furthermore, a small hump appeared around 15×10^3 cm^{-1} at 30 K. The temperature dependence of the first CT band resembles that of TTF-CA, which undergoes phase transition from neutral to ionic phase.[14] However, this complex is considered to be essentially neutral even at low temperature, because the second CT band, which should not be observed in the ionic ground state, still remains at 30 K.

In conclusion, the results shown here demonstrate that the degree of charge transfer of BD-TCNQ complex significantly increases on lowering temperature, by applying pressure, and probably by introducing intermolecular hydrogen bonds. However, all these perturbations does not bring out a change of the neutral BD-TDNQ complex to an ionic complex.

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