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Electronic Properties of One-Dimensional Iodine Complex. Benzo[*b*]phenothiazine-$I_{2.5}$

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One-dimensional metallic conductance was observed along the c axis of a single crystal of benzo[*b*]phenothiazine–iodine complex, $(B[b]PT)_2(I_3^-)(I)_2$, the crystal structure of which was preliminarily determined by X-ray analysis. Its metal-insulator transition was observed around 235 K, and the sign of the carriers seemed to be positive above 250 K. From the reflection spectra, with polarized light parallel to the c axis, a plasma-edge-like dispersion was observed in near IR region. Several parameters were evaluated by assuming a tight binding band model. The EPR spectra of this complex consist of only one broad signal (peak-to-peak width at room temperature 250×10^{-4} T) in the temperature range from 4 K to 296 K (g=1.998±0.002).

Since more than two decades, phenothiazine (PT) and its derivatives have been known to make semiconductive complexes with iodine.[1–15] None of them, however, has ever been structurally analyzed even if the complex was obtained as single crystals. Many reasons would be considerable about it. For example, there are so many crystallographically independent chemical entities in a large unit cell for 10-methylphenothiazine–iodine complex.[16] Moreover, PT derivatives–iodine complexes usually consist of several kinds of compounds having various mole ratios in spite of being composed of the same donor and acceptor.

We found that benzo[*b*]phenothiazine (B[*b*]PT) and iodine formed only one kind of complex compound with the composition, $(B[b]PT)_2(I_3)(I)_2$ (hereafter abbreviated as B[*b*]PT–$I_{2.5}$), and that it showed metallic behavior around room temperature and transferred to insulator at low temperature. This is the first case where metallic conduction has been observed among the complexes of PT derivatives. In this paper, we present the preliminary crystal structure, and electrical, magnetic, and optical properties of B[*b*]PT–$I_{2.5}$, and discuss the electronic structure and nature of the phase transition of this complex.

Experimental

B[*b*]PT was synthesized by the method of Van Allen et al.,[17] and purified by sublimation in vacuo (mp 291 °C, lit,[17] 278 °C). Commercially obtained iodine was also purified by sublimation.

Single crystals of B[*b*]PT–$I_{2.5}$ were prepared by diffusion method using a Y-shape tube with benzene as the solvent. The crystals were black prisms with metallic luster, having typical size of $0.5\times0.4\times1.0$ mm^3. Prior to each measurement described below, all the crystals were identified to be isostructural by X-ray photographs.

The electrical resistivity and thermoelectric power were observed over the range from 90 K to room temperature along the three crystal axes of single crystal. The resistivity along the most conductive c axis, growing direction, was measured by four-probe dc technique and those along the other two axes by two-probe technique. Carbon paint was applied as the contacts between electrodes (ϕ 30 μm gold wire) and crystal samples. In the case of thermoelectric power measurement, the electrodes were attached to two copper heat sinks, and the temperature difference between the sinks was controlled within 5 degrees.

The polarized reflection spectra were measured on the (010) crystal face for the incident light polarized parallel to the a and c axes. The measurement for the infrared region from 750 cm^{-1} to 6000 cm^{-1} was performed by using a Perkin–Elmer 1760-X FT-IR spectrometer and a Spectra-tech IR-PLAN$_{TM}$ infrared microscope. For the near-infrared and visible regions from 4500 cm^{-1} to 27500 cm^{-1}, measurements were carried out by using a Carl–Zeiss Universal microscope equipped Jobin-Yvon H-20V and H-20FIR monochromators. The spectra were calibrated for a gold evaporated mirror or a silicon crystal according to the observed regions.

EPR spectra for polycrystalline complexes were recorded over the temperature range of 4 K to 296 K using a JEOL JES-FE1XG X-band (9.1 GHz) EPR spectrometer equipped with an Air Products LTR 3-110 continuous-flow cryostat and Scientific Instrument Series 3700 digital temperature controller. Temperature was measured using a (0.07 at.% iron)-gold–chromel thermocouple, and controlled within 0.5 K. The g value was determined by comparing the resonance position with that of Mn^{2+}/MgO. The modulation width was kept much less than one-tenth of absorption line width during the measurements, in order to prevent distortion of line shape by overmodulation.

DSC for polycrystalline samples was measured from 173 K to 293 K with a Rigaku DSC-8240B at the scan speed of 1 deg min^{-1}.

Results and Discussion

Crystal Structure. The crystal data are as follows: $C_{16}H_{11}NS\cdot I_{2.5}$, F.W.=566.6, orthorhombic, *Pnmm*, a=13.976(1), b=17.824(1), c=6.434(1) Å, V=1602.7(3) Å^3,

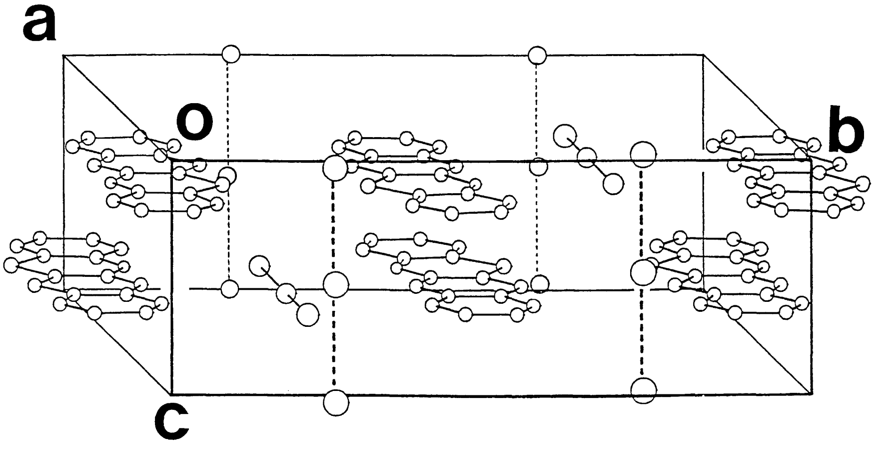

Fig. 1. The crystal structure of B[*b*]PT–$I_{2.5}$, a perspective view of the packing arrangement.

Table 1. Electrical Properties of B[*b*]PT–$I_{2.5}$

Direction	σ (300 K)/S cm^{-1}	S (300 K)/μV K^{-1}	E_a/eV
// a	3×10^{-2}	5×10^{1}	0.02
// b	2×10^{-2}	1×10^{2}	0.03
// c	3×10^{1}	3	Metallic

$Z=4$. At present, $R=0.061$ for 1133 reflections.[18] Figure 1 shows view of the crystal structure. The crystal consists of B[*b*]PT molecules, triiodide anions, and linear polyiodide chains. B[*b*]PT molecules, located on the crystallographic mirror plane [parallel to (001)], stack in face-to-face manner to form one-dimensional columns along the c axis. Spacing between B[*b*]PT planes is 3.22 Å, which is comparable with that of TTF, 3.47 Å in TTF-TCNQ.[19] There are two kinds of chemical species of iodine in this complex; one is linear I_3^- anion being parallel to the a axis, and the other is "linear polyiodide chain" being elongated along the c axis. The Fourier analysis indicates that one linear chain consists of iodine atoms arranging with almost equal intervals (3.207(6) and 3.227(6) Å, alternately).[20]

Electrical Conductivity and Seebeck Coefficient. The values of electrical transport properties of B[*b*]PT–$I_{2.5}$, summarized in Table 1, indicate that this complex is highly anisotropic and possesses one-dimensional character. Figure 2 shows temperature dependence of the electrical conductivity along the c axis. The conductivity slightly increases as temperature is lowered down to 235 K, where metal-insulator transition occurs. Below 200 K the conductivity decreases in an activated manner with a very small activation energy of $E_a=0.01$ eV. In the range 300—250 K, the Seebeck coefficient linearly falls with decreasing temperature and its extrapolation approaches zero at 0 K, as illustrated in Fig. 3. These results mean that B[*b*]PT–$I_{2.5}$ is in metallic state above 250 K. The positive values of Seebeck coefficient so far measured, suggest that the B[*b*]PT stacks are more conductive than the polyiodide chains.

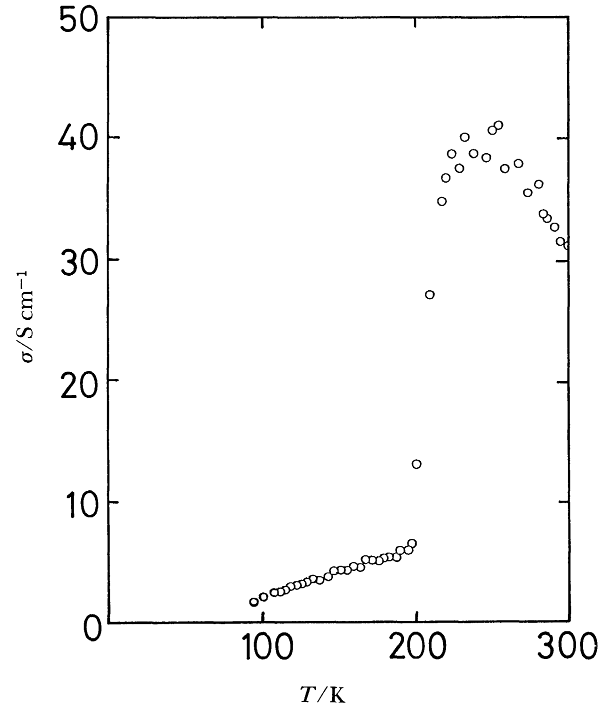

Fig. 2. Temperature dependence of electric conductivity of a single crystal of B[*b*]PT–$I_{2.5}$ measured along its c axis.

Polarized Reflection Spectra. Figure 4 shows the polarized reflection spectra of B[*b*]PT–$I_{2.5}$ at room temperature. The long-axes of both B[*b*]PT molecule and triiodide anion are parallel to the crystal a axis, as stated above, and the stacking direction of B[*b*]PT molecules and the linear chain direction of polyiodides are both parallel to the most conductive c axis. When the light polarization is parallel to the a axis, two sharp dispersions appear at 14500 and 25000 cm^{-1}. The former band (14500 cm^{-1}) can be assigned to the molecular excitation of B[*b*]PT cation radical polarized to the long axis of the molecule, as the band is also observed in the absorption spectrum of B[*b*]PT cation radical prepared by the electrochemical oxidation of B[*b*]PT in an acetonitrile solution.[21] The dispersion at 25000 cm^{-1} is safely assigned to the low-lying σ_g–σ_u* transition of triiodide anion.[22] When the incident light polarized parallel to the c axis, a plasma-edge-like dispersion appears in the near infrared region. So, it is confirmed that B[*b*]PT–I$_{2.5}$ is in metallic state at room temperature, as being in good agreement with the electrical measurements. In addition to this plasma-edge-like dispersion, a strong dispersion around 16000 cm^{-1} is observed in the //c spectrum. Since the polarization direction of this dispersion is parallel to the stacking direction of B[*b*]PT and/or polyiodide chain, the dispersion can be interpreted as the charge-transfer transition between iodide ions within the chain. Moreover, since the wavenumber of this band is lower than that of the isolated triiodide anion observed in the //a spectrum, the polyiodide would possess more stable electronic state than that of the isolated triiodide.

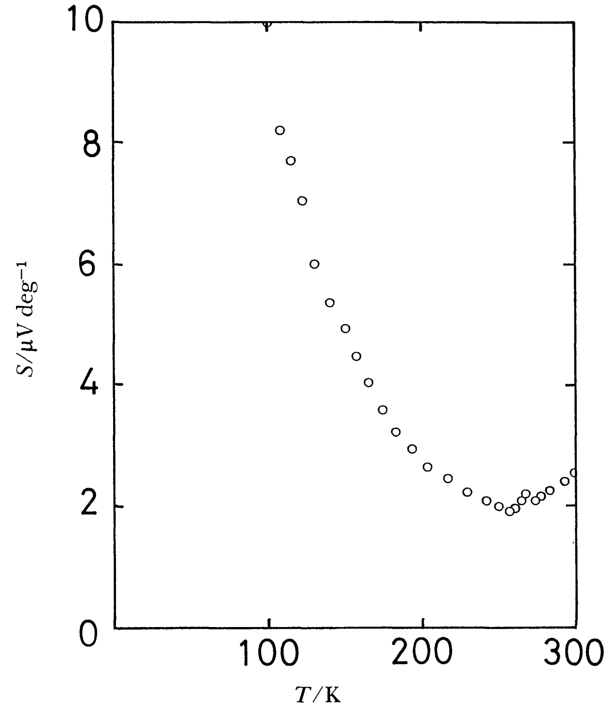

Fig. 3. Temperature dependence of Seebeck coefficient of a single crystal of B[*b*]PT–I$_{2.5}$ measured along its c axis.

Next, we have employed Drude-Lorentz model to analyze the //c spectrum assuming Lorentz oscillator around 16000 cm^{-1}. This procedure consists of the following dielectric function;

$$\varepsilon(\omega)=\varepsilon_{\text{core}}-\frac{\omega_p^2}{\omega(\omega+i\tau)}-\frac{f_1}{\omega(\omega+i\tau_1)-\omega_1^2}, \tag{1}$$

where ω_p is the plasma frequency, f_1 is the oscillator strength, $\varepsilon_{\text{core}}$ is the residual dielectric constant at high frequency, and τ and τ_1 are the relaxation time of carriers and the oscillator, respectively. For the analysis of the //c spectrum, we adopted only the reflectance spectrum from 1900 to 27500 cm^{-1}, since the reflectance spectrum of the region lower than 1900 cm^{-1} would be influenced by intramolecular

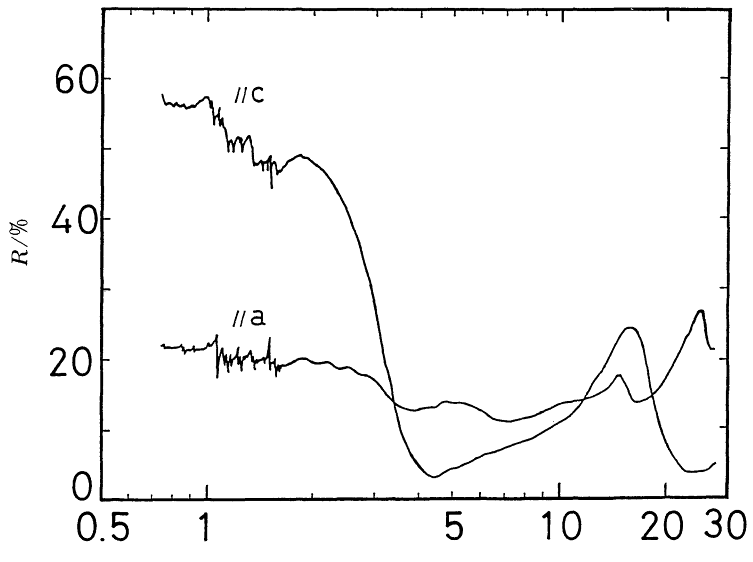

Fig. 4. Polarized reflection spectra of B[*b*]PT–I$_{2.5}$.

vibration of B[*b*]PT and/or coupling up the vibration to conduction electron. By assuming a tight-binding band, the experimentally evaluated parameter ω_p may be related to the tight-binding band width 4t by the equation.

$$\omega_p^2 = \frac{16tNe^2d^2\sin(\pi\rho/2)}{h^2}, \qquad (2)$$

where N is the number density of molecules, ρ is the number of carriers per molecule, and d is the molecular period along the polarization direction of incident light. ω_p may also be related to the optical effective mass m^* and optical conductivity at zero frequency σ_{opt} (0) by the following equations,

$$\omega_p^2 = \frac{4\pi ne^2}{m^*} = \frac{4\pi\sigma_{opt}(0)}{\tau}, \qquad (3)$$

where n is the number density of free carriers. For the tight-binding band, the Fermi velocity V_F and the mean free path Λ are derived from $4t$ and τ by the equations,

$$V_F = \frac{2td}{h}, \qquad \Lambda = V_F\tau. \qquad (4)$$

By using the values N=2.50×10^{21} cm^{-3}, d=3.22 Å, and ρ=0.5, assumed that there are equal numbers of neutral and cation radical B[*b*]PT molecules in the crystal, the transport parameters are calculated from these equations by the analysis of the //c spectrum. They are summarized in Table 2 with the corresponding data of $(\text{perylene})_2(\text{PF}_6)_{1.1}\cdot0.8\text{CH}_2\text{Cl}_2$[23] and TTF-TCNQ[24-26]. B[*b*]PT-$\text{I}_{2.5}$ represents intermediate values of ω_p and 4t between those of them, and it suggests that B[*b*]PT-$\text{I}_{2.5}$ has intermediate property between them.

EPR Measurement. It was observed that the EPR spectra of B[*b*]PT-$\text{I}_{2.5}$ consisted of only one signal, and its shape was slightly asymmetric Lorentzian under all the observed temperature range from 4 K to 296 K. At room temperature the observed peak-to-peak linewidth ΔB, 250 G (1 G=10^{-4} T), is rather broad as an aromatic cation radical including sulfur.[27-29] The g-value was found to be 1.998±0.002, being slightly smaller than that of free electron. Both values imply that there is an interaction between the radical electron on B[*b*]PT cation radical and iodine atoms, because the latter has a large spin-orbit coupling constant. Magnetic susceptibilities obtained from the EPR intensity is 1×10^{-4} emu mol^{-1} at 296 K. Figure 5 illustrates the temperature dependence of the magnetic susceptibility. Below 50 K the susceptibility nearly follows Curie's low, and above this temperature it behaves in an activated manner with a slight change around 235 K. Since this temperature agrees with that of metal-insulator transition observed in the electrical measurement, it is suggested that the magnetic property of this complex also changes around 235 K. Judging from no discontinuous change in the temperature dependence of susceptibility around this temperature, the metal-insulator transition would not be a first-order phase transition. In the very low temperature region, the observed susceptibility was assumed to come from paramagnetic impurities, the contribution of which was estimated ($C=\chi/T$, C=17 emu mol^{-1}) and shown by solid line in Fig. 5. Deducting this contribution from observed susceptibilities, the activation energy was found to be 0.06±0.02 eV. The peak-to-peak linewidth ΔB increases approximately linearly with temperature up to 300 K, as shown in

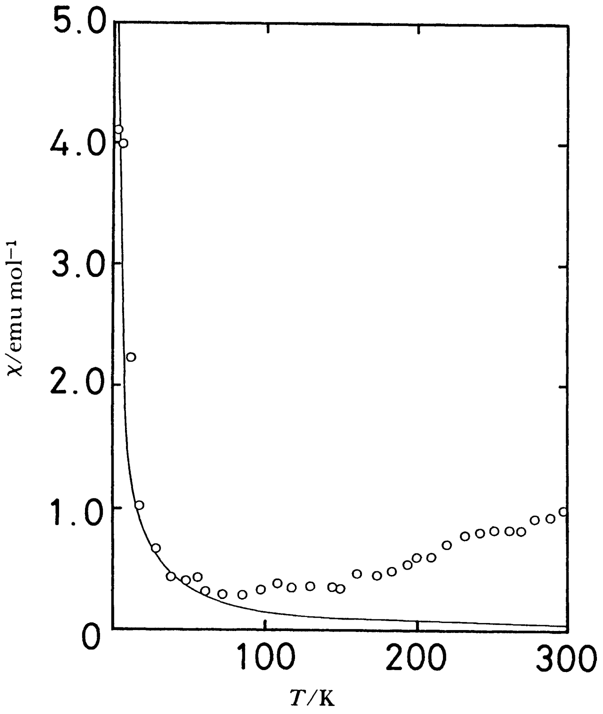

Fig. 5. Temperature dependence of magnetic susceptibility of B[*b*]PT-$\text{I}_{2.5}$.

Table 2. Transport Parameters Obtained from the Analysis of the Reflectance Data

Compound	$\omega_p/2\pi$	τ	n	m^*/m_e	$4t$	Λ	$\sigma_{opt}(0)$
	cm^{-1}	10^{-15} s	10^{21} cm^{-3}		eV	Å	S cm^{-1}
$(\text{Pe})_2(\text{PF}_6)_{1.1}\cdot0.8\text{CH}_2\text{Cl}_2$	(7400)	4.4	1.42	0.91	1.1		1900
B[*b*]PT-$\text{I}_{2.5}$	7720	2.9	1.25	1.9	0.87	4.3	550
TTF-TCNQ	9500	4	2.8	3	0.43		1200

The value derived from their data is given in parentheses.

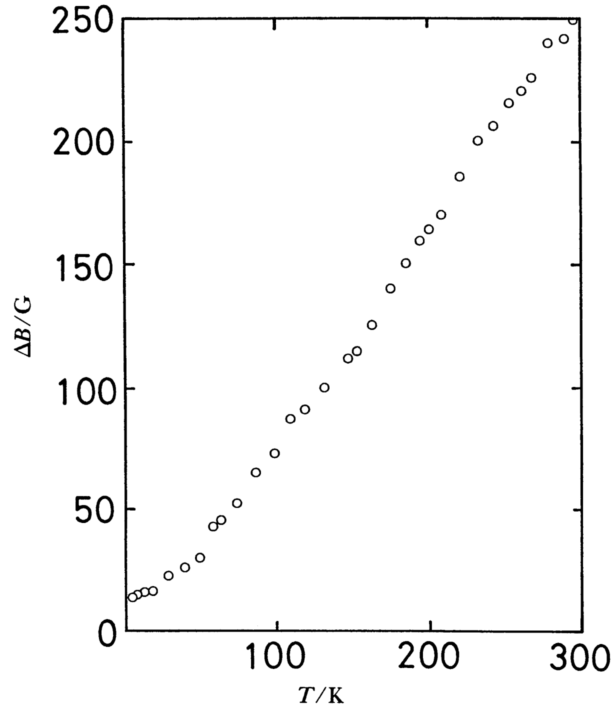

Fig. 6. The EPR peak-to-peak line width vs. temperature observed about B[*b*]PT–$I_{2.5}$.

Fig. 6, although a slight change in slope appears around 235 K. This temperature corresponds to that observed when the temperature dependence of the susceptibility was measured.

DSC Measurement. DSC measurements showed neither endothermic nor exothermic peak around 235 K. Therefore, it was found that the metal-insulator transition observed in the measurement of electrical properties was not first-order transition with latent heat.

Summary and Conclusions

B[*b*]PT–$I_{2.5}$ exhibits a metallic state in the high temperature phase, but has electrical and magnetic activation energies in the low temperature phase. The transition temperature was observed around 235 K. However, no discontinuous change of the magnetic susceptibility and the EPR linewidth, and no latent heat on DSC measurements were observed around the transition temperature. These facts would imply that the transition is attributed to the Peierls-type transition around 235 K. The electronic state of B[*b*]PT would be a mixed state of cation radical and neutral one. However, a quantitative estimation of this mixed state is hardly established, since the information about electronic state of the linear polyiodide chain is insufficient at this stage.

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