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Electrical Conductivity of Hexaiodobenzene and Tetrahalo-*p*-benzoquinone under Very High Pressures

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The electrical resistances of hexaiodobenzene, iodanil, bromanil, and chloranil have been studied under very high pressures. The lowest resistivity at 500 kbar is about 5 Ω-cm for hexaiodobenzene and 5×10^{-2} Ω-cm for iodanil. This difference may be mainly explained by the charge transfer from iodine to oxygen atoms in the latter compound.

Introduction

During the past decade, the effect of the pressure on the electrical conductivities of polycyclic aromatic crystals has been studied. Their conductivities at about 200 kbar increase to $10^4 \sim 10^{10}$ times those at atmospheric pressure (*1–3*). These abrupt changes are caused by the overlapping of π electron clouds of adjacent aromatic molecules.

In a previous paper (*4*), we reported that the pressure dependence of the electrical resistance of microcrystals of iodanil is quite large; the least resistivity is 5×10^{-2} Ω-cm at about 500 kbar. This observed value of the resistivity is quite low in the group of polycyclic aromatic semiconductors at high pressure. The anomalous electrical behavior indicates that the interatomic interactions between adjacent molecules may be increased significantly. The contact of O---I and I---I between adjacent molecules would be very important for electrical conduction.

In this paper we will present some results on the electrical properties of hexaiodobenzene (C_6I_6), iodanil ($C_6I_4O_2$), bromanil ($C_6Br_4O_2$), and chloranil ($C_6Cl_4O_2$) under very high pressures and we will discuss their electrical conduction.

Experimental

Conductivity measurements were carried out using a split-sphere apparatus constructed at Osaka University (*5*). The details of the sample arrangement and pressure calibration have been described elsewhere (*6*).

The materials used in the experiment were as follows. Hexaiodobenzene was prepared by the reaction of iodine with benzene and 60% anhydrous sulfuric acid at 170 ~ 180°C (*7*). This stable compound was purified by a method of vacuum sublimation The compositions of C_6I_6 were determined by elemental analysis Chloranil and bromanil were purified by recrystallizations and by fractional sublimation. Iodanil was prepared by the reaction of bromanil with potassium iodide in hot alcohol (*8*). This compound was recrystallized from ethyl acetate.

The electrical resistance of polycrystalline pellets of these compounds was measured under very high pressure.

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Results and Discussion

Hexaiodobenzene. This compound crystallizes in space group $P2_1/c$ with two molecules in a unit cell (*9*). Crystal data are summarized in Table I. The molecular packing in the crystal is determined by the I---I contacts between adjacent molecules, most of which are shorter than the sum of the van der Waals radii, 4.30 Å. The shortest intermolecular distance of I---I is about 3.74 Å. Figure 1 shows the resistance versus pressure curve for C_6I_6. The electrical resistivity decreases monotonously toward 5 Ω-cm, up to the highest applied pressure available in the present vessel. The resistivity of the evaporated film of this compound is found to be about 10^{14} Ω-cm, with an energy gap of about 1.6 eV at atmospheric pressure. The resistance decreases by a factor of approximately 10^{13} in 500 kbar at room temperature. Since the C atoms are shielded by the bulky iodine atoms, the large change of the resistance with pressure must arise from the increase of I---I contacts.

It has been reported (*10*) that I_2 and SnI_4 crystals show metallic behavior at high pressure. Iodine molecules crystallize in an orthorhombic form with the molecules arranged in the planar sheets parallel to the *ac*-plane. The shortest intermolecular distance is 3.54 Å in the *ac*-plane. The intermolecular distance between adjacent layers is 4.03 Å, which is slightly shorter than the sum of the van der Waals radius of iodine. The iodine crystal is an insulator at 1 atm. The electrical resistivity indicates the large anisotropy, 2×10^{11} Ω-cm (perpendicular to the *ac*-plane), and 6×10^7 Ω-cm (in the *ac*-plane). The resistivity of the single crystal decreases rapidly with increasing pressure and the activation energy becomes zero in the *b* direction at 160 kbar and in the *ac*-plane at 220 kbar (*11*). It should be noted that the transition pressure to the metallic state in the *b* direction is lower than that in the *ac*-plane. This may arise from the large compressibility of *b*-axis direction. The linear compressibility of the *b*-axis is very large compared with that of the *a*- and *c*-axes; $b/b_0 = 0.81$ but a/a_0 and $c/c_0 = 0.905$ at 200 kbar (*10*). This suggests that the overlapping of $5P_z$ electrons between adjacent layers increases remarkably with increasing pressure.

SnI_4 crystallizes in a cubic lattice with eight molecules per unit cell. The shortest intermolecular distance of I---I is 4.30 Å, twice the van der Waals radius of the iodine atom. However, SnI_4 is extremely compressible:

TABLE I

Crystal Data of Halogen-Substituted Benzene Derivatives

Compound		Crystal data		
Chloranil, $C_6Cl_4O_2$	$P2_1/a$	$a = 8.707$	$b = 5.755$	$c = 8.603$[a]
		$\beta = 105.51°$	$Z = 2$	
	(C^5_{2h})	$a = 8.86$	$b = 5.83$	$c = 8.76$[b]
		$\beta = 72.6°$	$Z = 2$	
Bromanil, $C_6Br_4O_2$	$P2_1/a$	$a = 8.62$	$b = 6.17$	$c = 9.02$[b]
		$\beta = 74.2°$	$Z = 2$	
Iodanil, $C_6I_4O_2$	$P2_1/c$	$a = 7.630$	$b = 5.268$	$c = 14.222$[c]
		$\beta = 113.07°$	$Z = 2$	
Hexaiodobenzene, C_6I_6	$P2_1/c$	$a = 8.85$	$b = 4.28$	$c = 18.08$[d]
		$\beta = 116.30°$	$Z = 2$	

[a] Ref. (*11*).
[b] Ref. (*10*).
[c] Ref. (*12*).
[d] Ref. (*8*).

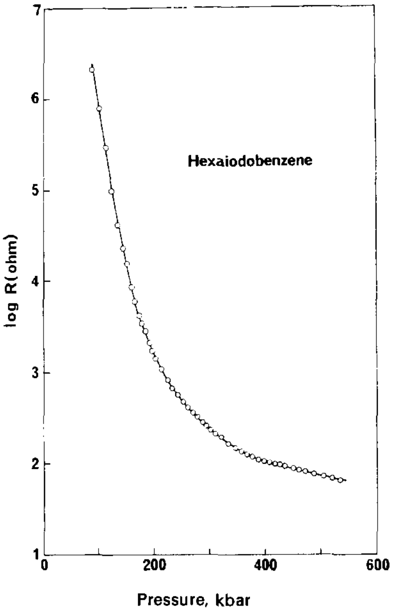

FIG. 1. The pressure dependence of the electrical resistance of hexaiodobenzene at room temperature.

The relative volume is reduced to 0.528 at 200 kbar (*10*). Therefore, this compound shows metallic behavior at high pressure.

Though the electrical resistance of C_6I_6 decreased rapidly with increasing pressure, the metallic behavior was not observed up to 500 kbar. The average intermolecular distances of I---I in a C_6I_6 crystal are shorter than those of SnI_4, but are longer than those of I_2. The compressibility of C_6I_6 has not been measured, but it is probably comparable to that of aromatic hydrocarbons. From the relation between the pressure and the volume for molecular solids given by Samara and Drickamer (*1*), the average intermolecular distance at 500 kbar was estimated to be about 85% of that at atmospheric pressure. The intermolecular distances of I---I in C_6I_6 at very high pressure are much longer than those of metallic iodine. Judging from the crystal structure, it is expected that the *b*-axis is more compressible than that of *c*- and *a*-axes. The interplanar distance is 3.86 Å. The distance is expected to become about 3.3 Å at 500 kbar. However, this is longer than the I---I distance of metallic iodine. C_6I_6 molecules are not planar in the crystal (*9*). The overlapping between the nearest C_6I_6 molecules is not very large; therefore, metallic behavior of C_6I_6 is not observed, even at very high pressure.

Chloranil and bromanil. Figure 2 shows the pressure dependence of the electrical resistance of chloranil and bromanil. The resistance of chloranil was insensitive to pressure. On the contrary, the resistance of bromanil decreased with increasing pressure above 200 kbar. Chloranil and bromanil are isomorphous. There are two molecules in the unit cell and the space group is $P2_1/a$ (C_{2h}^5) (*10, 11*). Crystal data are summarized in Table I. The crystal of chloranil consists of two layers of substituted halogen atoms which are parallel to the (001) plane, and the skeletons consisting of oxygen and carbon atoms lie between these two layers (*12*). The intermolecular distances of Cl---Cl and Cl---O are longer than the sum of the van der Waals radii. The short intermolecular separation from a carbon to an oxygen, 2.85 Å, has been observed (*13*). The electrical behavior at high pressure was not affected by the anomalous short distance. In the case of bromanil, the intermolecular distances of Br---Br and Br---O are longer than the sum of the van der Waals radii. The

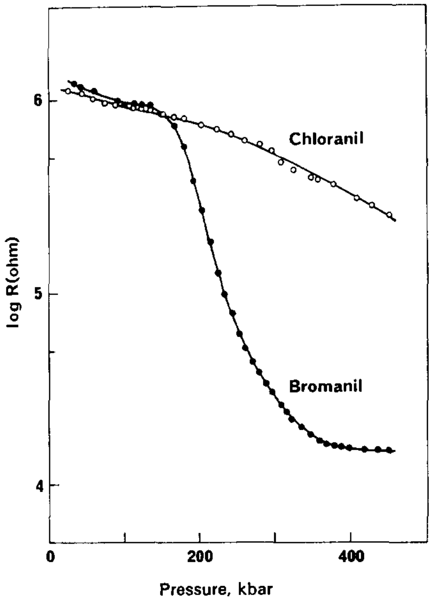

FIG. 2. The pressure–resistance curve of chloranil and bromanil.

anomalous short distance has not been reported. The change of the resistance above 200 kbar may arise from the increase of Br---Br contacts with pressure.

Iodanil. This compound crystallizes in space group $P2_1/c$ with two molecules in a unit cell (*14*). The molecular packing in the crystal is determined by the I---I contacts between adjacent molecules. The shortest intermolecular distance of I---I is about 3.79 Å, which is slightly longer than that of C_6I_6. Figure 3 shows the projection of the structure along the *b*-axis. The iodanil molecules are stacked to form columns along the *b*-axis, with an interplanar distance of 3.694 Å. The degree of overlap of nearest molecules is not very large. As is shown in Fig. 3, it should be noted that there is one unusually short contact between iodine and oxygen atoms (γ(I---O) = 3.23 Å). The O---I distance is 0.32 Å shorter than the sum of the van der Waals radii. Figure 4 shows the absorption spectra of iodanil at atmospheric pressure. The absorption spectra of the evaporated films show two maxima, whereas only one maximum is observed in the spectra of benzene solution (7×10^{-5} *M*). The electronic state of an iodanil molecule in the crystalline state differs from that of an isolated molecule. The difference may be attributable to intermolecular interactions in the crystalline state. In the complex of iodine and oxygen

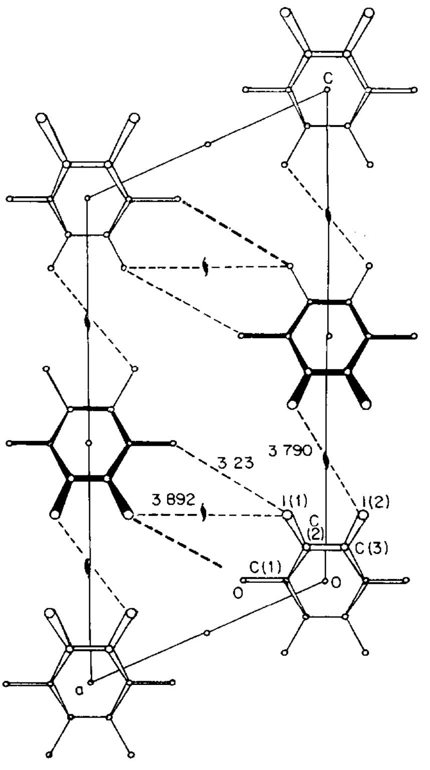

FIG. 3. Projection of the structure along the *b*-axis.

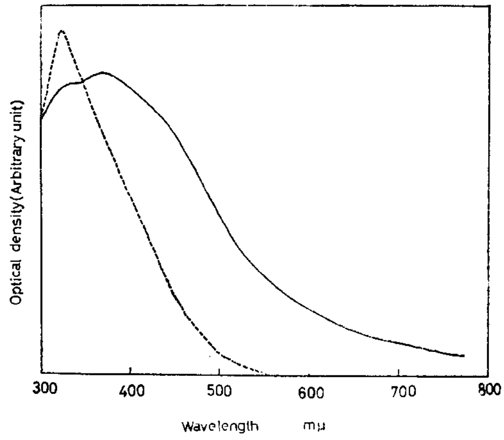

FIG. 4. The absorption spectra of iodanil. ——, evaporated film; ---, benzene solution.

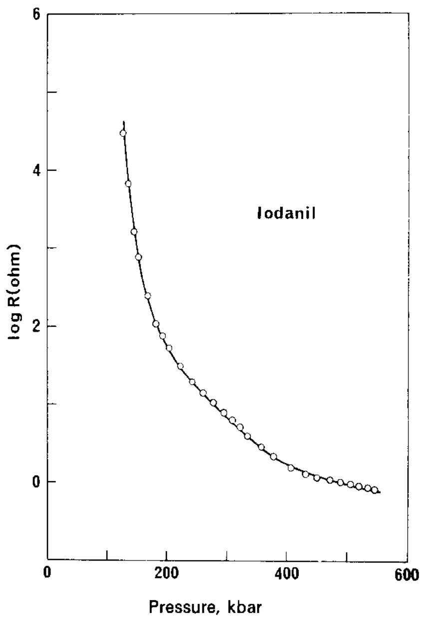

FIG. 5. The electrical resistance of iodanil as a function of pressure.

molecules, the charge transfer band has been found around 435 ~ 470 nm (*15*). The absorption band of iodanil in the acetone solution depends strongly on its concentration. The intensity of absorption above 400 nm increased with the increase in the concentration. These results suggest that the broad band at longer wavelength is mainly due to the charge transfer absorption spectrum arising from the interaction between iodine and oxygen atoms. The values of electronegativity of iodine and oxygen are 3.0 and 2.2, respectively. This large discrepancy suggests that the charge transfer interaction between oxygen and iodine is very important.

The resistivity of a single crystal along the *b*-axis is 10^{12} Ω-cm, with an energy gap of about 1.37 eV at atmospheric pressure. Figure 5 exhibits the resistance versus pressure curve for the microcrystal of iodanil. The resistance decreases continuously by a factor of approximately 10^{13} with increasing pressure up to 500 kbar. The resistivity at 500 kbar is 5×10^{-2} Ω-cm. This value is 100 times lower than that of C_6I_6. Since the I---I distances of both iodine compounds are nearly equal, the difference of the resistivity at 500 kbar may arise mainly from the charge transfer from iodine to oxygen atoms. The transition to the metallic state was not observed at this pressure. As the O---I distance is shortened with pressure, the charge transfer interaction increases under high pressure. If the electron is transferred from the filled band of iodine to oxygen, this band may be partially empty. Therefore, it is to be expected that this compound would have metallic behavior at very high pressure.

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