The Effect of Pressure on the Semi-conductivity of Isoviolanthrone

By Hiroo INOKUCHI

(Received April 18, 1955)

On the semiconductive properties of violanthrene and related polycyclic aromatic compounds reports have been presented in the previous papers[1,2]. Since the preparations of single crystals of those compounds are very difficult and the specimens are obtained in powdered form, the measurements of electrical resistivity were usually made under compressed states. In such a condition, the apparent resistivity is likely to depend strikingly upon the compressive pressure. The relation between resistivity and pressure up to 300 kg./cm^2 has been reported in a preceding paper[3]. The results showed that resistivity decreases remarkably with increasing pressure up to 80 kg./cm^2; however, thereafter it becomes approximately constant. A similar result was also reported by D. D. Eley et al.[4] For this and other reasons, we have assumed that the observed resistivity is an intrinsic one, excluding the contact resistance between the crystalline particles, when measurement was made beyond 80 kg./cm^2.

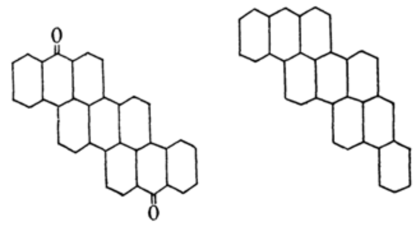
There is an interesting point concerning the pressure effect on the conductivity of organic semi-conductors. Polycyclic aromatic compounds are made of a typical molecular lattice, wherein the intermolecular force is none other than van der Waals type and not so great as compared with that in ionic or valence bond crystals. From the measurements of the heat of sublimation, the intermolecular force is found to depend on the molecular weight and 30.2 kcal./mol. for perylene and 52.3 kcal./mol. for violanthrene[5]. The compressibility is not known; however, it is presumably rather high*.

Therefore, it could be presumed that when these organic semi-conductors are compressed under high pressure, the molecules would be brought nearer to each other than the equilibrium positions and this is accompanied by further overlapping of the electron clouds (diffuse π-orbitals) or every molecule; this would have an effect on the semi-conductivity.

In this paper the effect of hydrostatic pressure up to 8,000 kg./cm^2 is presented.

Experimental Procedures

Among the condensed polycyclic aromatic compounds, violanthrene ($C_{34}H_{18}$) and isoviolanthrone ($C_{34}H_{16}O_2$) were selected for measurements (Fig. 1). These samples were purified as already described[5], and made into a rod, 2 mm. diameter and 6 mm. height, under ca. 300 kg./cm^2 pressure. This rod was supported by copper wire in a silicon oil as is shown in Fig. 2. In order to prevent silicon oil from flowing out from a gap between piston and cylinder, this contact was made carefully air-tight. Subsequently, this rod



isoviolanthrone violanthrene

Fig. 1. Isoviolanthrone and violanthrene.

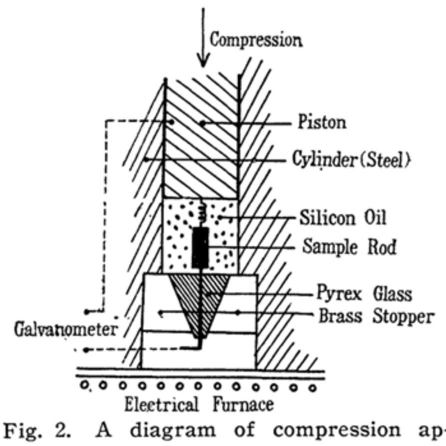


Fig. 2. A diagram of compression apparatus.

1) H. Akamatu, *Kagaku* (Iwanami), 282 (1954).
2) H. Inokuchi, This Bulletin, 24, 222 (1951); 25, 29 (1952); 27, 22 (1954).
3) H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, 18, 810 (1950).
4) D.D. Eley et al., *Trans. Farad. Soc.*, 49, 79 (1953).

* The compressibility of benzene (solid) and naphthalene is $20\sim30\times10^{-6}$ (range 100 kg./cm^2~1,000 kg./cm^2 compression)[7,8], then the volume change is 2% of its initial value under 1,000 kg./cm^2.

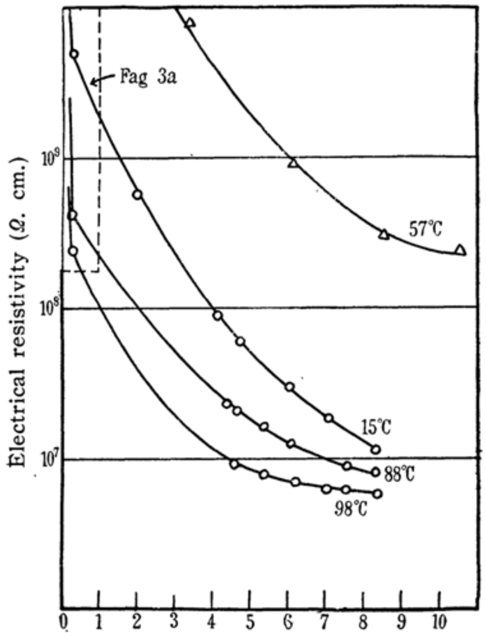
5) H. Inokuchi, S. Shiba, T. Handa and H. Akamatu, This Bulletin, 25, 299 (1952).
6) H. Akamatu and K. Nagamatsu, *J. Colloid Sci.*, 2, 593 (1947).
7) T.W. Richards et al., *J. Am. Chem. Soc.*, 43, 1538 (1921).
8) H. Essex, *Z. anorg. Chem.*, 88, 200 (1914).

was compressed by hydrostatic power with hydraulic press.

Since the compressed specimen has pretty good conductivity, the conductivity measurement was made directly without using D.C. amplifier. To know the temperature dependency of conductivity, samples were heated by electrical furnace from a room temperature up to 130°C as shown in Fig. 2.

Results and Discussion

The electrical resistivity of these organic semi-conductors decreased with compression above 300 kg./cm². The resistivity of isoviolanthrone was lowered to one five-hundredth of its value at an ordinary compression (under 80 kg./cm²~300 kg./cm² pressure). This relation is shown in Fig. 3. This dec-

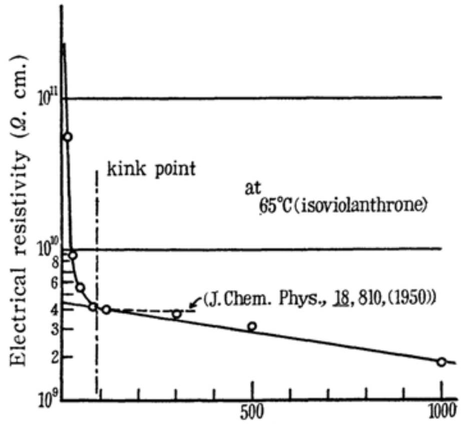


Pressure kg./cm²

Fig. 3. The relation between electrical resistivity (ρ) and pressure (p).
△ Violanthrene
○ Isoviolanthrone

rease of resistance is of the same order as in the case of phosphorus[9] or selenium[10], that is, the decrease of resistivity of the former being to 1/1000 of its initial value with 20,000 kg./cm² compression, and that of the latter being to 1/50~1/200 under 3,000 kg./cm².

As shown in Fig. 3a, the resistivity-pressure relation curve seems reasonably to divide into two parts. The former one (I) has a deep descent between the pressure

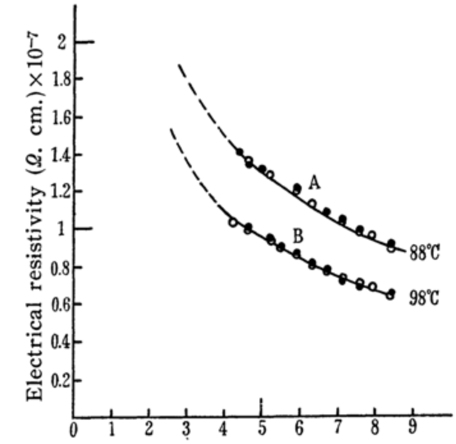


Pressure kg./cm²

Fig. 3a. The ρ-p curve between the pressure range of 0 to 1,000 kg./cm².

range of 0 to 80~100 kg./cm² and the latter part (II) has a mild descent above the pressure of 80~100 kg./cm². The kink point of this curve is coincident with one in which electrical resistivity is constant against pressure approximately[3]. Then it seems to be possible to suppose that the curve (I) is due to the plastic deformation of a specimen with the increasing pressure and latter part (II) is an elastic deformation of the compound.

Therefore, for the reason mentioned above, it seems that the intrinsic value of electrical resistivity of this group is obtained by the extrapolation of the curve (II) at the section of the axis of pressure 0 kg./cm². This value is coincident approximately with the observed one of electrical resistivity under 80 kg./cm² ~300 kg./cm² compression, and these results are consistent with the previous reports[3].



Pressure kg./cm²

Fig. 4. The reversible curve of ρ-p relation of isoviolanthrone.
○ increasing pressure
● decreasing pressure

9) P.W. Bridgman, *Proc. Nat. Acad. Sci.*, **21**, 109 (1935).
10) F. Montén, Diss., Upsala (1909).

The change of resistivity was quite reversible to the pressure. Fig. 4 shows this relation between the electrical resistivity and the pressure from 3,000 kg./cm^2 to 8,000 kg./cm^2. From this relation, I think also that the observed decrease of electrical resistivity is an intrinsic one due to the elastic deformation of crystals, but not due to the change of crystal packing nor to any other plastic deformation.

The temperature dependency of the electrical resistivity (ρ) of these specimens has the semi-conductive character, that is,

$$\rho = \rho_o \exp(\Delta\epsilon/2kT) \quad (1)$$

where k is the Boltzmann's constant, T is the absolute temperature and $\Delta\epsilon$ is the activation energy. $\Delta\epsilon$, corresponds to the energy gap between the occupied level and the empty level, decreased too with increasing pressure, but as shown in Table I the change was rather small.

TABLE I
THE VALUE OF $\rho_{15°}$ AND $\Delta\epsilon$ OF ISOVIOLANTHRONE WITH A COMPRESSION

Compression kg./cm^2	$\rho_{15°}\Omega$. cm.	$\Delta\epsilon$ kcal./mol.	$\Delta\epsilon$ e.V.
3×10^2	5×10^9	17.3	0.75
4.2×10^3	8.4×10^7	17.0	0.74
6.3×10^3	2.6×10^7	15.9	0.69
8.4×10^3	1.2×10^7	15.0	0.68

From the above results, the author inclines to assume that the increment in electrical conductivity with high pressure is contributed by electron clouds overlappings between molecules in the molecular lattice.

If the elastic constants of these organic crystals are known, and if these compounds are more compressed, we may have very interesting results.

Summary

The electrical resistivity of isoviolanthrone ($C_{34}H_{16}O_2$) and violanthrene ($C_{34}H_{18}$) decreased with compression. The resistivity of isoviolanthrone was lowered to 1/500 of its value (5×10^9 Ω.cm.) at an ordinary pressure, that is, 8.4×10^7 Ω.cm. at 4.2×10^3 kg./cm^2 and 1.2×10^7 Ω.cm. at 8.4×10^3 kg./cm^2 at 15°C. Further it is possible to suppose that the observed decrement of electrical resistivity is an intrinsic one, due to elastic deformation of crystals.

The author desires to express his hearty thanks to Prof. H. Akamatu for his kind direction of this study. The cost of this research has been defrayed from the Grant in Aid for Fundamental Scientific Research from the Ministry of Education, to which the author's thanks are also due.

Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo