The Electrical Conductivity of the Condensed Polynuclear Aromatic Compounds

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Introduction

In the previous paper,(1) the electrical conductivity of violanthrone, isoviolanthrone and pyranthrone has been reported. These substances belong to the condensed polynuclear aromatic compound. The electrical conductivity of these substances has been attributed to π-electrons of the conjugated double bonds of network-plane of carbon atoms. The highest limit of this network-plane is graphite, which has the electrical resistivity of 10^{-3} Ωcm. (powdered state). On the other hand, the electrical resistivity of benzene, the lowest limit of these substances, is higher than 10^{18} Ωcm.

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(1) H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950).

in the solid state. Therefore the electrical conductivity of these compounds in the solid state are closely corelated to the numbers of rings which are contained in the network-planes, and also to the π-electrons of these molecules. From this standpoint, the study has been extended over a series of compounds belonging to this group.

Experimental Procedure

Because the single crystals could not be obtained, eleven samples of this group, described below, were examined in the state of compressed powdered form. For the higher conductive substances, the method has been already described, apparatus-I, which was like that used by Brunner and Hammerschmid for measuring the conductivity of powdered graphite.(1),(2),(3) In this method, the specimen was compressed between the metal end and piston in the polished ebonite cylinder of good quality or ambroide cylinder, and the electrical resistivity was measured by the potential drop method with the aid of direct current amplifier.

For the lower conductive substances, another apparatus was used (Fig. 1: apparatus-II). The specimen was compressed on a cylindrical dish, which was made of brass coated by chromium, by a piston to 80 kg./cm.^{2} with a lever system. This piston was insulated by ambroide (1) (5) and pyrex glass (4). The electrical resistivity observed depends, in the first approximation, on the area of the end of the piston, which is 0.503 cm.^{2}. This apparatus has an advantage over the former in regard to the problem of the effects of the temperature and surface leakage. The surface leakage could be avoided and the temperature could be increased to 300°, because the ebonite cylinder was not used.

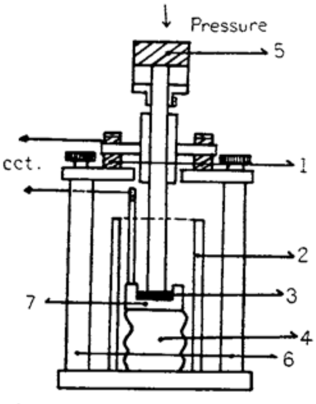

Fig. 1.—Apparatus-II: (1) and (5) ambroide insulated a piston; (2) electrical oven, shielded by copper plate; (3) specimen; (4) pyrex glass; (6) brass; (7) cylindrical dish, coated by chromium.

In the previous paper,(1) it was found that in each case the constancy of the electrical conductivity of these powdered specimens is obtained when the compressed pressure upon them is over 80 kg./cm.^{2}. This fact was supported again in the following manner.

The electrical conductivity of anthanthrene ($C_{22}H_{12}$: m. p. 257.5°-258°) was measured by the apparatus-II under 80 kg./cm.^{2} pressure. The temperature was increased to 264°, above the melting point of this crystal, and then decreased to the room-temperature. The hysteresis of electrical conductivity upon the increasing and decreasing of temperature was almost negligible (Fig. 2). This fact shows that the contact resistance between the powdered crystals was not affected practically under 80 kg./cm.^{2} or more in pressure. Therefore, the value of electrical conductivity measured by these methods was assumed to be intrinsic.

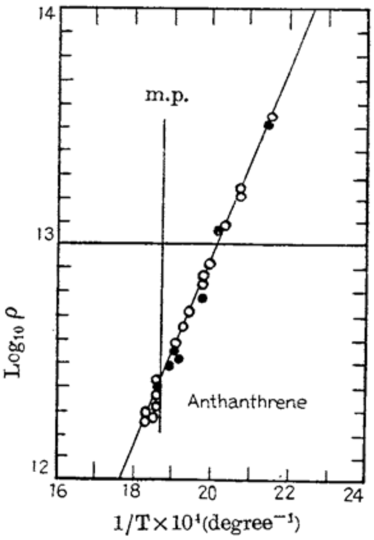

Fig. 2.—The relation between resistivity and temperature for anthanthrene by the apparatus-II: ○ 80 kg./cm.^{2}, before melted; ● 80 kg./cm.^{2}, after melted.

The samples were purified chemically(4) and then sublimed in vacuum (10^{-2}-10^{-5} mm. Hg.) more than two times until the conductivity was constant. The vacuum sublimation is an extremely advantageous method; the impurities—starting substances, by-products and carbonious matters etc.—were completely separated in the manner just like chromatography, and also there was no trace of solvent between crystals at all.

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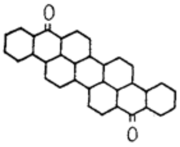
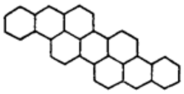
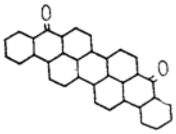
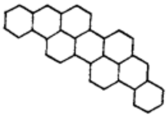
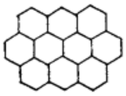
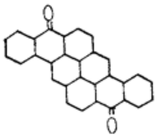
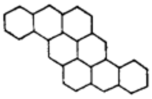
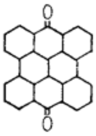
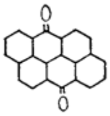
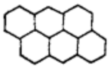
(2) H. Akamatu and H. Inokuchi, *J. Chem. Soc. Japan*, **70**, 185 (1949).

(3) J. Brunner and H. Hammerschmid, *Z. Electrochem.*, **40**, 60 (1934).

(4) H. Akamatu and K. Nagamatsu, *J. Colloid Sci.*, **2**, 593 (1947).

Table 1

The Value of ρ_{15}, $\Delta\epsilon$ and ρ_0 of the Condensed Polynuclear Aromatic Compounds.

No.	Substance	Structure	ρ_{15}, Ωcm.	$\Delta\epsilon$, e. V.	ρ_0, Ωcm.
1	Isoviolanthrone		5.7×10^{9}	0.75	1.5×10^{3}
2	Isoviolanthrene		8.4×10^{13}	0.82	6.3×10^{6}
3	Violanthrone		2.3×10^{10}	0.78	2.9×10^{3}
4	Violanthrene		2.1×10^{14}	0.85	6.85×10^{6}
5	Ovalene		2.3×10^{15}	1.13	3.1×10^{5}
6	Pyranthrone		3.9×10^{15}	1.06	3.7×10^{6}
7	Pyranthrene		4.5×10^{16}	1.07	2.0×10^{7}
8	Meso-naphthodianthrone		1.5×10^{18}	1.30	6.0×10^{6}
9	Meso-naphthodianthrene		4.0×10^{18}	1.2	1.8×10^{8}
10	Anthanthrone		7.7×10^{18}	1.70	9.7×10^{3}
11	Anthanthrene		1.5×10^{19}	1.67	3.4×10^{4}

Results and Discussion

The names and colours of solid specimens used are;

(1) isoviolanthrone (dark green), (2) isoviolanthrene (red), (3) violanthrone (violet), (4) violanthrene (dark red), (5) ovalene (reddish-orange), (6) pyranthrone (orange-red), (7) pyranthrene(brown), (8) meso-naphthodianthrone (greenish-yellow), (9) meso-naphthodianthrene (dark green), (10) anthanthrone (scarlet) and (11) anthanthrene (brownish-yellow). Their molecular structures were illustrated in Table 1.

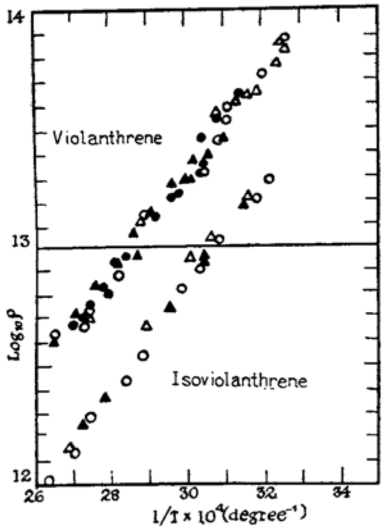


Fig. 3a.—The relation between resistivity and temperature for violanthrene and isoviolanthrene by the apparatus-I: △ 82.1 kg./cm.^{2}, rising temperature; ▲ 82.1 kg./cm.^{2}, falling temperature; ○ 119.5 kg./cm.^{2}, rising temperature; ● 119.5 kg./cm.^{2}, falling temperature.

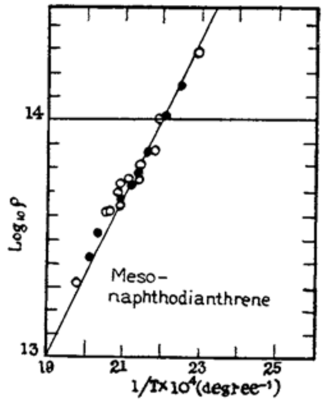


Fig. 3b.—The relation between resistivity and temperature for meso-naphthodianthrene (apparatus-II): ○ 80 kg./cm.^{2}, rising temperature; ● 80 kg./cm.^{2}, falling temperature.

The logarithm of electrical resistivity $\log\rho$ and the reciprocal of temperature $1/T$ have the linear relation as in the case of violanthrone etc.,

$$\rho=\rho_0 \exp(\Delta\epsilon/2kT). \qquad (1)$$

Some examples of this relation are illustrated on Figs. 2 and 3. The value of ρ_0, ρ at 15° (extrapolated value), and $\Delta\epsilon$ are shown in Table 1.

The good reproducibility of electrical resistivity against temperature, non-effect from the moisture and independency of the current upon the time proved the electronic conduction. We think these substances to be the electronic semi-conductor from the characteristics of Eq. (1), and this assumption is also supported by the fact that violanthrone and violanthrene, for example, have the sensitive photoconductivity which is now under investigation. As these organic compounds are prefect molecular crystals, we cannot consider the possibility of impurity-level such as in the cases of CuS or PbS.

For these reasons they must be intrinsic semi-conductors. In Table 1 it is found that the electrical conductivity is increased together with the numbers of π-electron or the conjugated double bonds in molecule, and $\Delta\epsilon$, corresponding to the energy difference between the empty level and the occupied level of the crystal on the model of semi-conductors, is decreased with the increasing of the numbers of π-electron in the molecule.

To confirm the contribution of π-electron to the electrical conductance, the conductivity of Hydro-violanthrene (yellow), which was made by the strong reduction from violanthrone by the red phosphorus and hydrogen iodide, was measured by the apparatus-II. The numbers of the π-electron of this substance are decreased by the strong reduction illustrated as Fig. 4, and also the mobility of electrons will be restricted in the molecule. The measurement was carried out under 80 kg./cm.^{2} in pressure and heated above 250°, over the melting point of this compound.

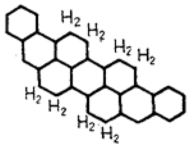


Fig. 4.—The structure of hydro-violanthrene.

Compared with the other compounds, the result of temperature-resistivity relation was the same, Fig. 5, but the difference of energy band, $\Delta\epsilon$, and extrapolated resistivity to 15°, ρ_{15}, have exceedingly higher value. These results were tabulated on Table 2 with violanthrone and violanthrene. It is shown by this result that the existence of π-electrons in these substances leads to electrical conductance.

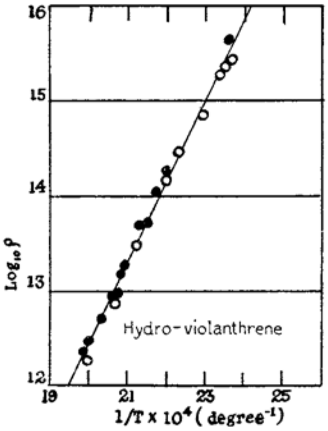


Fig. 5.—The relation between resistivity and temperature for hydro-violanthrene: the same symbols as in Fig. 3b.

Table 2

The Value of ρ_{15}, ρ_0 and $\Delta\epsilon$ of Hydro-violanthrene, Violanthrene and Violanthrone.

	Hydro-vilanthrene	Violanthrene	Violanthrone
Colour	yellow	dark red	violet
ρ_{15}, Ωcm.	1.1×10^{25}	2.1×10^{14}	2.3×10^{10}
ρ_0, Ωcm.	3.0×10^{-5}	6.85×10^{6}	2.9×10^{3}
$\Delta\epsilon$, e. V.	3.4	0.85	0.78

The quinonoid structures of this group lead to a great increase of electrical conductivity as compared with its hydrocarbons, but the intervals of energy band, $\Delta\epsilon$, have the same value. And in comparsion with the magnetic susceptibility of this group, it is interesting to note that the electrical conductivity was not affected greatly by the shape of the molecule, but by the numbers of π-electron alone.

Summary

The electrical conductivity of the condensed polynuclear aromatic compounds; (1) isoviolanthrone, (2) isoviolanthrene, (3) violanthrone, (4) violanthrene, (5) ovalene, (6) pyranthrone, (7) pyranthrene, (8) meso-naphthodianthrone, (9) meso-naphthodianthrene, (10) anthanthrone and (11) anthanthrene,—has the character of a semi-conductor. The resistivity of these compounds can be expressed as $\rho=\rho_0 \exp(\Delta\epsilon/2kT)$. The value of $\Delta\epsilon$ and ρ at 15° were found as, (1) 0.75 e. V., 5.7×10^9 Ωcm., (2) 0.82 e. V., 8.4×10^{13} Ωcm., (3) 0.78 e. V., 2.3×10^{10} Ωcm., (4) 0.85 e. V., 2.1×10^{14} Ωcm., (5) 1.13 e. V., 2.3×10^{15} Ωcm., (6) 1.06 e. V., 3.9×10^{15} Ωcm., (7) 1.07 e. V., 4.5×10^{16} Ωcm., (8) 1.30 e. V., 1.5×10^{18} Ωcm., (9) 1.2 e. V., 4.0×10^{18} Ωcm., (10) 1.70 e. V., 7.7×10^{18} Ωcm., (11) 1.67 e. V., 1.5×10^{19} Ωcm.. The good reproducibility and non-hysteresis of the electrical conductivity for temperature suggests electronic conduction. As these organic compounds have a perfect molecular lattice, the possibility of impurity-level cannot be considered. For this reason the mechanism of the conduction is assumed to be that of the intrinsic semi-conductor.

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