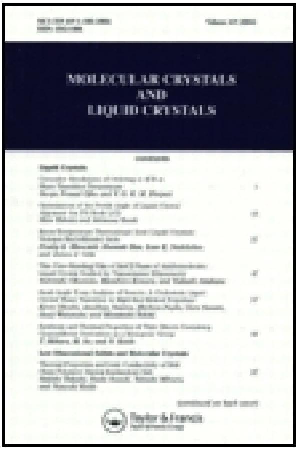

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Studies of Organic Semiconductors for 40 Years—II
Polycyclic Aromatics as Organic Semiconductors

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In Japan, the initiation of the studies of organic semiconductors was the work on carbons materials such as graphite and carbon black.

CARBON MODEL

In the period from 1940 ~ 1945, the research group in Sameshima's laboratory, Department of Chemistry, University of Tokyo, was studying the physico-chemical properties of carbons. The structures of carbons in which carbon atoms are bonded together in various manners were not at all understood in the mid 1940's. However, it was already known that the basic structure of carbons is condensed aromatic hydrocarbons, that is six-membered benzene rings. Realizing that these condensed polycyclic aromatic compounds can be considered to be ultra-micro-crystallites of carbons, Akamatu and Nagamatsu prepared carbon-like structures from polycyclic aromatic type vat-dyestuffs, violanthrone, isoviolanthrone and pyranthrone, by mixing their sulphuric acid solutions followed by aggregation in water.[1]

To prepare the carbon-like aggregates, the mixing of different molecular sizes of polycyclic aromatics was essential. By this "carbon synthesis" the existence of many sorts of carbons could be explained by the sizes of the component aromatic hydrocarbons and the mode of two dimensional molecular aggregation.

PHYSICO-CHEMICAL PROPERTIES OF GRAPHITIZATION

In Sameshima's laboratory, a systematic investigation of the graphitization processes of carbons by their heat-treatment up to 3000°C was carried out. Structural changes which occurred during the graphitization process were examined by X-ray diffraction and electron microscopy.

The electrical conductivity[2] and magnetic susceptibility of graphite and also carbon black as a function of the graphitization process was also studied.

During the observation of the electrical conduction of graphitized carbon particles, it was considered that the electron transport from one carbon particle to another should resemble that from one molecule to another molecule in a molecular crystal.

ELECTRICAL CONDUCTION OF ORGANIC SOLIDS

It was decided that a measurement of the electrical conduction of polycyclic aromatic compounds should be made, and in particular one of the typical "carbon model" compounds. We selected violanthrone, isoviolanthrone and pyranthrone as examples of the polycyclic aromatic compounds.[3] (Figure 1)

The first difficulty of this conductivity work was the purification of the samples. Crude samples were dissolved in concentrated sulphuric acid and the solution was poured into a large amount of water under 10°C with strong stirring. The precipitated specimen was filtered, washed to remove acid and dried at 100°C. Further, the samples were sublimed in vacuum ($10^{-2} \sim 10^{-5}$ mmHg) several times until the conductivity was constant.

The second difficulty of this work was that "the specimen was powder". At that time, we did not consider making a single crystal of these polycyclic aromatic compounds. Thus the conductivity measurement was carried out in the state of a compressed powdered form. The specimen was packed in a good quality ebonite cylinder and compressed between the metal ends. The electrical resistance was measured by the current produced for a known applied potential giving not over 800 v/cm.

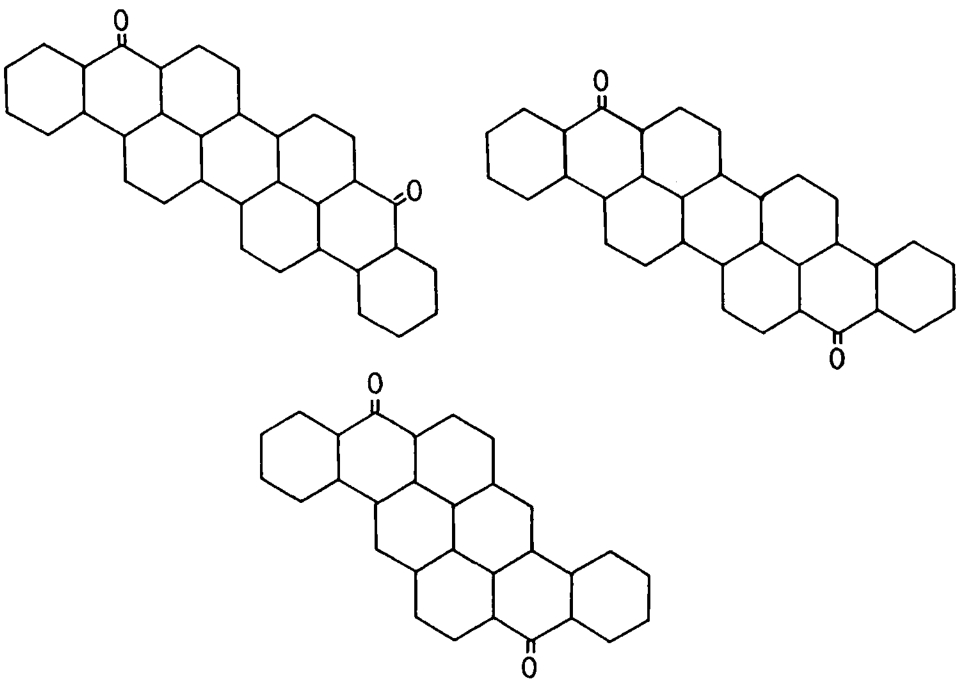

FIGURE 1 Violanthrone, iso-violanthrone and pyranthrone.

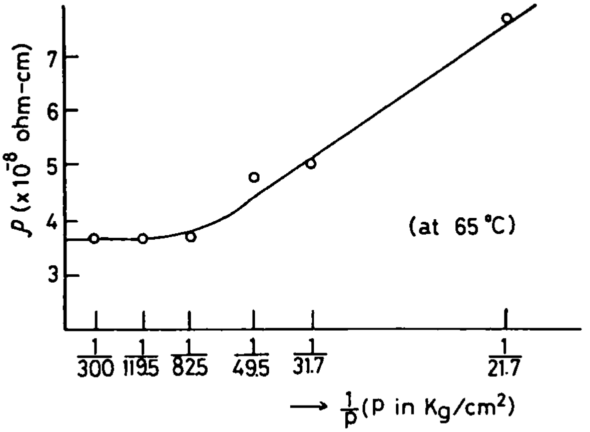

FIGURE 2 The relation between resistivity and pressure for iso-violanthrone.

To eliminate the effect of contact resistance, we observed the electrical resistivity as a function of pressure.

Figure 2 gives the relation between electrical resistivity and pressure p. At that time, we assumed the resistivity was approximately constant above 80 Kg/cm^2.

The temperature (T) coefficient of the electrical resistivity (ρ) was negative in every case, with a linear relation between log ρ and $1/T$ corresponding to $\rho = \rho_0 \exp(E/kT)$, where E is the activation energy. Values of E, and of ρ at 10°C are given in Table I and Figure 3.

Electrical conduction of polycyclic aromatics as a function of condensation of benzene rings

From the feeble electrical conduction of violanthrone, isoviolanthrone and pyranthrone, we expected that the electrical conductivity was due to π-electrons of the conjugated double bonds in the network-plane of carbon atoms. We considered that the highest limit of this network-plane was graphite and the lowest limit of these substances was benzene. It was imagined that the electrical conductivity of these compounds in the solid state was closely correlated to the number of rings which are contained in the network-planes, and also to the π-electrons of these molecules.[4]

TABLE I

The value of ρ at 15°C ρ_0, E and $\Delta\epsilon$ ($\sigma = \sigma_0 \exp(-\Delta\epsilon/2kT)$) of violanthrone, iso-violanthrone and pyranthrone

	Violanthrone	Iso-violanthrone	Pyranthrone
ρ(15°C)	2.3×10^{10} Ωcm	5.7×10^{9} Ωcm	3.9×10^{15} Ωcm
E	0.39 eV	0.375 eV	0.53 eV
σ_0	3.4×10^{-4} $\Omega^{-1}cm^{-1}$	6.8×10^{-4} $\Omega^{-1}cm^{-1}$	4.7×10^{-7} $\Omega^{-1}cm^{-1}$
$\Delta\epsilon$	0.78 eV	0.75 eV	1.06 eV

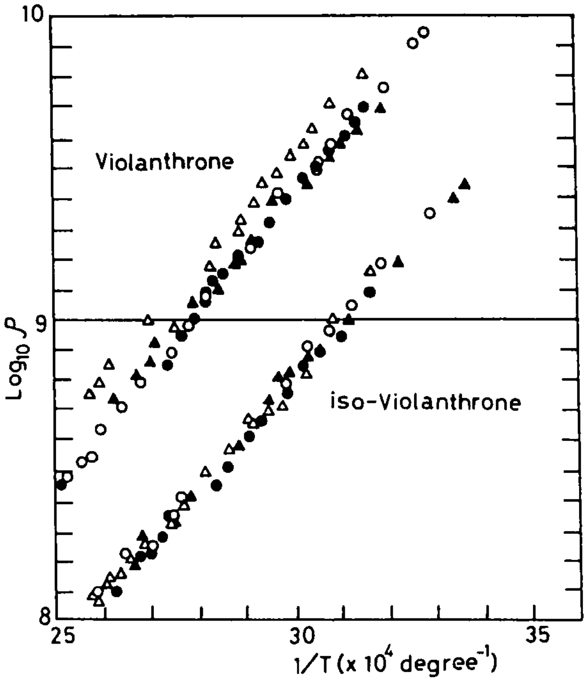

FIGURE 3 The relation between resistivity and temperature for vilanthrone and iso-violanthrone. Δ82.1 Kg/cm², rising temp. ▲82.1 Kg/cm², falling temp. ○119.5 Kg/cm² rising temp. ●119.5 Kg/cm² falling temp.

Table II summarises the values of ρ_0, ρ at 15°C and for various kinds of polycyclic aromatics from the relation $\rho = \rho_0 \exp(\Delta\epsilon/2kT)$.

To confirm the contribution of π-electron density of the molecule to the electrical conductance, the conductivity of the yellow-coloured hydrocarbon, hydro-violanthrene (Figure 4), which was prepared by red phosphorus and hydrogen iodide, was measured by a similar method. The results are tabulated in Table III with

TABLE II

The value of ρ(15°C), $\Delta\epsilon$ and ρ_0 of the condensed polynuclear aromatic compounds

Substance	ρ(15°C)Ωcm	$\Delta\epsilon$ eV	ρ_0Ωcm
Isoviolanthrone	5.9×10^{9}	0.75	1.5×10^{3}
Isoviolanthrene	8.4×10^{13}	0.82	6.3×10^{6}
Violanthrone	2.3×10^{10}	0.78	2.9×10^{3}
Violanthrene	2.1×10^{14}	0.85	6.85×10^{6}
Ovalene	2.3×10^{15}	1.13	3.1×10^{5}
Pyranthrone	3.9×10^{15}	1.06	3.7×10^{6}
Pyranthrene	4.5×10^{16}	1.07	2.0×10^{7}
Meso-naphthodianthrone	1.5×10^{18}	1.30	6.0×10^{6}
Meso-naphthodianthrene	4.0×10^{18}	1.2	2.8×10^{8}
Anthanthrone	7.7×10^{18}	1.70	9.7×10^{3}
Anthanthrene	1.5×10^{19}	1.67	3.4×10^{4}

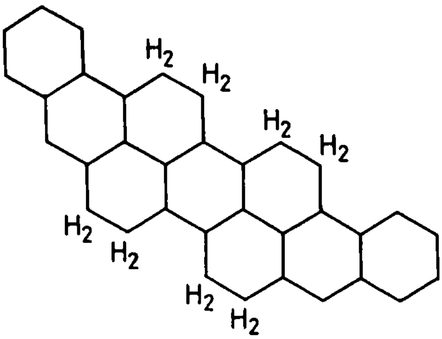

FIGURE 4 Hydro-violanthrene.

those of violanthrone and violanthrene. It is shown by this result that the existence of π-electrons in these substances leads to electrical conductance.

PHOTOCONDUCTION OF THE VIOLANTHRONE SERIES

From the conductivity measurements of the polycyclic aromatic series, it was determined that these organic compounds appeared to be semiconductors. To confirm this electronic conduction of organic solids, we investigated the photoconductivity of violanthrone series.[5]

In this experiment, we used an evaporated film of the organic crystals. The detailed description of preparation of photocell is as follows: Two pieces of thin tin foil, 10mm in width, were stuck on a quartz plate with a gap between them of 1mm. The film of violanthrone or isoviolanthrone was deposited by vaccum evaporation between the foils. The increase in conductivity produced by illumination was measured in terms of current changes for a constant potential difference between the foils.

We found a photoelectric current produced by the illumination of monochromatized light from a 500 watt tungsten lamp. The photocurrent decreases with the wavelength of the incident radiation in each case, and a threshold is found as shown in Figure 5.

The value of light quantum in eV at each threshold is shown in Table IV.

TABLE III

The value of $\rho(15°C)$, ρ_0 and $\Delta\epsilon$ of hydro-violanthrene, violanthrene and violanthrone

	Hydro-violanthrene	Violanthrene	Violanthrone
Colour	yellow	dark red	violet
$\rho(15°C)\Omega cm$	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}
$\Delta\epsilon$ eV	3.4	0.85	0.78

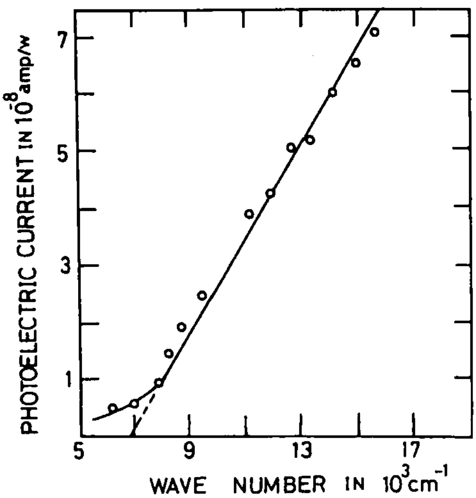

FIGURE 5 Photoconductive response of violanthrone.

DENOTATION OF ORGANIC SEMICONDUCTORS

In the next step, we accumulated the experimental results of photoconduction of various kinds of polycyclic aromatics. Then, in 1954, we presented to the Bulletin of the Chemical Society of Japan the denotation of "organic semiconductors" as follows.[6]

In previous works, we have reported that violanthrone, isoviolanthrone and pyranthrone have photoconductivity and intrinsic semiconductor characters. Similar behaviour was found for the other related compounds, that is, the condensed polynuclear aromatic and aza-aromatic compounds. For example, indanthrone black ($C_{34}H_{14}N_2O_2$) has an electrical resistivity of 2.5×10^8 Ωcm and ovalene ($C_{32}H_{14}$) has 2.3×10^{15} Ωcm. Such particular pure compounds as these have never found in measurements of the electrical conductivity of many sorts of compounds. Also this group of compounds shows luminescent character by the action of cathode-ray and ultra-violet light in the solid state. These properties can be attributed to the intermolecular overlappings of the electron clouds of π-electrons in the polynuclear condensed aromatic rings.

TABLE IV

The threshold value of photoconductivity

	Violanthrone	Iso-violanthrone	Pyranthrone
Threshold wave Number	6.8×10^3 cm^{-1}	7.5×10^3 cm^{-1}	9.22×10^3 cm^{-1}
Energy gap form Photoconductivity	0.84 eV	0.93 eV	1.14 eV
Energy gap from Thermal Activation Energy	0.78 eV	0.75 eV	1.06 eV

Up to the present, the research of semiconductors has been mostly restricted to the field in the branch of semiconductive materials. We may call these organic compounds-organic semiconductors.

Since then, we started to apply the term "organic semiconductors" to the group of conjugated double bond compound such as polycyclic aromatics and phthalocyanines.

At the same time, the discovery of the unusual electrical properties of the "perylene-bromine complex" had been made in the same department.[7] The details of this work will be described by Y. Matsunaga in these proceedings.

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