On the Electrical Conductivity of the Organic Thin Films: Perylene, Coronene and Violanthrene

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In recent years, the electronic conduction in organic compounds has aroused interest and a number of reports on their related behaviors have been accumulated[1,2]. The early works in this field were of the preliminary survey type, but recent articles tend to concentrate on the physico-chemical properties of the specific compounds under more carefully controlled conditions. However, some substantial discrepancies are still found in the results observed by different investigators. Some of the discrepancies may be due to the difference in the preparation or the formation of the specimens. For instance, thin evaporated films of aromatic hydrocarbons are frequently applied to the investigation of the semi- and photo-electrical conductivity. However, relatively little attention has been given to the structure of these films.

The present paper deals with the electrical conductivity and structural survey of thin organic films prepared in vacuo upon various substrates.

Experimental

Materials.—*Coronene (I).*—This aromatic compound, including a small amount (nearly 5%) of higher condensed aromatic compounds, was provided

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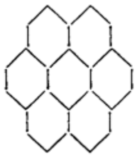
[1] H. Akamatu and H. Inokuchi, "Proceedings of the Third Conference on Carbon", Pergamon Press, London (1959), p. 51.

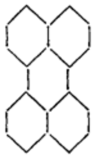
[2] C. G. B. Garrett, "Semiconductors", (N. B. Hannay, ed.), Reinhold, New York (1959), p. 634.

by Badische Anilin and Soda Fabrik A. G. in Germany[3]. First, the crude hydrocarbon was purified carefully by means of the recrystallization method from its benzene solution. In addition, through the repeated high vacuum sublimations, pure coronene, for which the melting point was 438°C, was separated as a beautiful yellow hydrocarbon[4].

Perylene (II) and Violanthrene (III).—These two polycyclic aromatic hydrocarbons were synthesized by Drs. T. Handa and J. Aoki. The purified hydrocarbons were obtained by evaporation in vacuo in a manner similar to that reported in the previous article[5].



(I)



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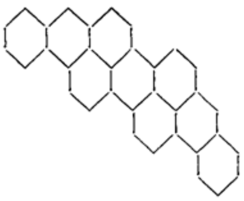

(III)

Procedures.—The following three types of conductivity cells were employed to measure the electrical resistivity of the organic compounds.

The Sandwich-type Cell.—The aromatic hydrocarbons having approximately one or two microns in thickness was deposited by vacuum evaporation on a pyrex glass plate, which had been coated in advance with aluminium film to provide one electrode. A second electrode, thereafter, was formed by evaporation of aluminum film under a high vacuum as shown in Fig. 1. The electrical resistivity of this cell was measured in an atmosphere of argon. The estimation of specific resistivity was not so accurate, because of large errors incurred in the observation of the dimensions of the specimens.

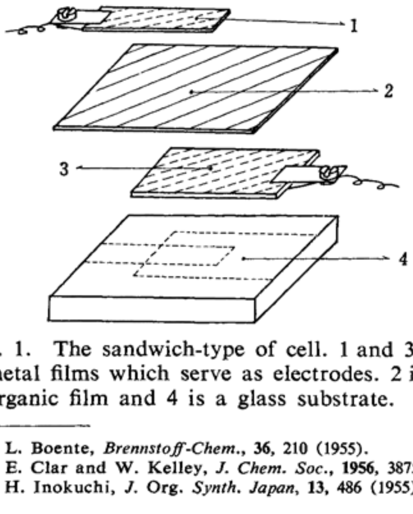

Fig. 1. The sandwich-type of cell. 1 and 3 are metal films which serve as electrodes. 2 is an organic film and 4 is a glass substrate.

The Surface-type Cell. — This type of cell was prepared by evaporation of an organic film on a pyrex glass plate which has parallel electrodes that are separated from each other by a gap of 2 mm. This cell was placed in a glass chamber as shown schematically in Fig. 2. These electrodes were connected through two metal-to-glass seals to the vibration-reed electrometer. Throughout all the experiments, this chamber was maintained in a vacuum of 10^{-5} mmHg or less, to preclude an effect of air and/or of humidity on the films*.

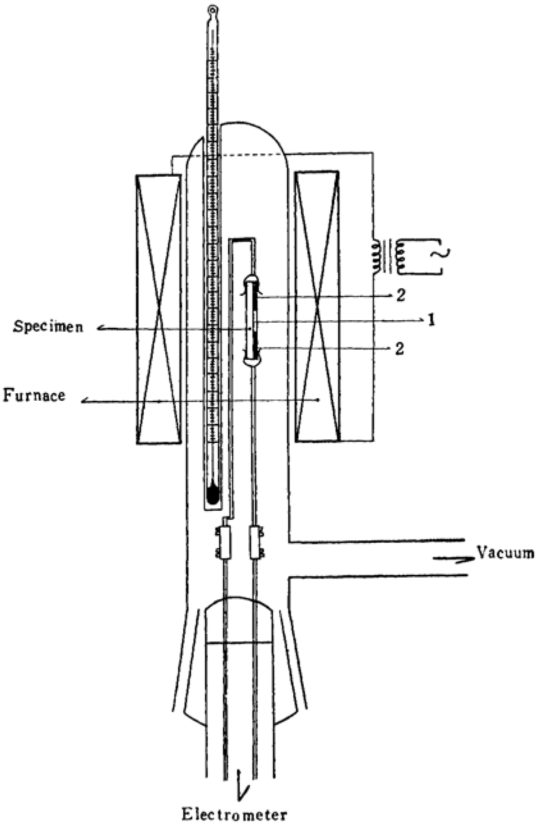

Fig. 2. The surface-type of conductivity cell placed in a glass chamber.
1, Organic thin layer
2, Terminal electrode

The Bulk Specimen.—The crystalline powders were packed into a quartz cylinder, area 0.5 cm², between two platinum-plated brass electrodes. The specimens were compressed in the cylinder up to 116 kg./cm² by a lever system.

Technique.—*Electric Conduction.*—The resistances of the above specimens, at room temperature, were from 10^9 to $10^{14}\,\Omega$. The measurements of high resistance were carried out, therefore, with the

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[3] L. Boente, *Brennstoff-Chem.*, **36**, 210 (1955).

[4] E. Clar and W. Kelley, *J. Chem. Soc.*, **1956**, 3875.

[5] H. Inokuchi, *J. Org. Synth. Japan*, **13**, 486 (1955).

* From a preliminary experiment, an introduction of air into the chamber is one of the most important reasons for the instability of the conductivity of thin films and also one of the interesting aspects of their studies.

association of the vibration-reed electrometer apparatus.

X-Ray Diffraction.—The transparent organic films evaporated on several substrates—glass, potassium chloride crystal, copper plate and also the cleavage surface of graphite—were examined as to their textured structures by means of a Geiger counter X-ray diffractometer.

Electron Micrograph.—The electron micrographs were made with association of the Hitachi electron-microscope, HU-10. The structural analysis of the small individual crystals ($1\,\mu \times 1\,\mu$) in the thin organic films could be carried out easily by means of the electron microdiffraction combined with the electron micrograph. As a specimen for the above two methods, the transparent organic films on glass substrates were stripped off from the substrates and in addition the carbon-replica technique was applied on them.

Results and Discussions

Through all the experiments, the results of the electrical resistivity of various types of conductivity cells can be expressed by a semi-conductive equation[1] (Fig. 3):

$$\rho = \rho_0 \exp(\Delta\varepsilon / 2kT)$$

where $\Delta\varepsilon$ is an apparent energy gap. The various forms of specimens with regard to the type of cells are thus compared with each other conveniently in terms of $\Delta\varepsilon$ and the electrical resistivity ρ at 15°C in Table I.

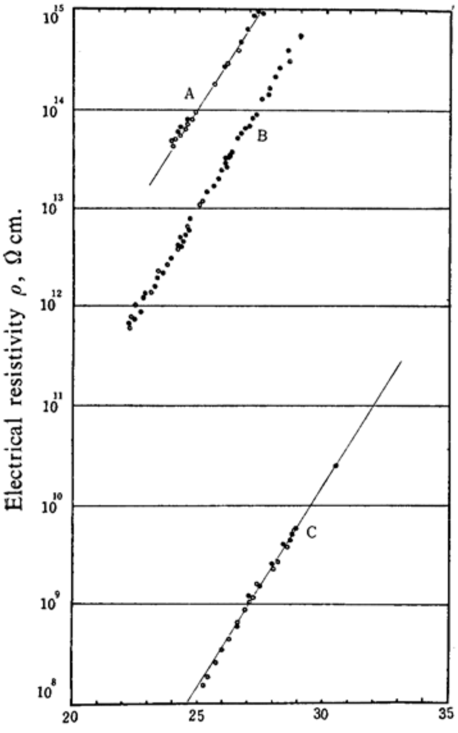


Fig. 3. The electrical resistivity versus temperature of various types of violanthrene conductivity cells.
A. Sandwich-type B. Bulk C. Surface-type

TABLE I. THE ELECTRICAL RESISTIVITY OF POLYCYCLIC AROMATICS, OBSERVED FROM THE VARIOUS TYPES OF CELL

Compound	Perylene	Coronene	Violanthrene
From bulk specimen			
ρ_{15}(Ω cm.)	4×10^{18}	1.7×10^{17}	2.1×10^{14}
$\Delta\varepsilon$(eV.)	2.0	1.7	0.85
From surface-type cell			
ρ_{15}(Ω cm.)	$\sim10^{13}$	$10^{12}\sim10^{13}$	$\sim10^{9}$
$\Delta\varepsilon$(eV.)	2.2	1.65	0.9
From sandwich-type cell			
ρ_{15}(Ω cm.)	$10^{18}\sim10^{19}$	$10^{17}\sim10^{18}$	$\sim10^{14}$
$\Delta\varepsilon$(eV.)	2.0	1.6	0.9

In this table, it is found that the electrical resistivity observed with the sandwich-type cell is in quite good agreement with that of the bulk specimen. However, a great difference is found between the resistivities of the sandwich-type cell and the surface-type one. The resistivity of the sandwich-type cell is much less than that of the surface-type by a factor of $10^4\sim10^5$. The electric field is applied along the surface of the film in the surface-type cell, while it is applied perpendicularly to the film for the sandwich-type cell. Therefore, the difference implies that there is an anisotropy of resistivity in the thin film.

It is well known that when a substance is deposited onto a substrate from solution or vapor phase to produce a thin film, a textured

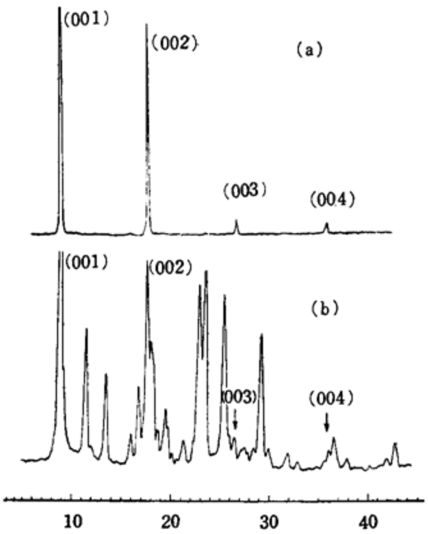
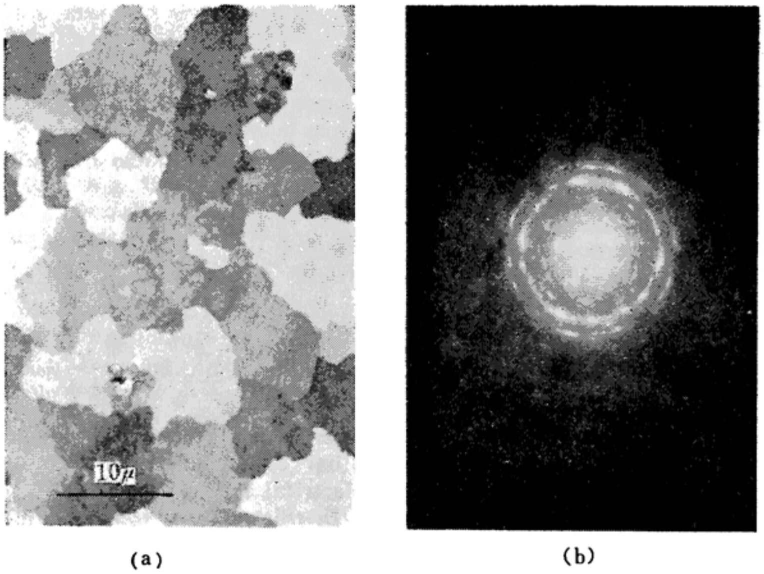


Fig. 4. The X-ray diffractometer records of (a) powder and (b) evaporated film of coronene.



(a) (b)

Fig. 5. (a) The electron micrograph and (b) the electron microdiffraction pattern of an evaporated film of coronene.

structure in which crystallites are arranged with a preferred orientation usually occurs. This was proved for the evaporated film of the aromatic compounds by means of X-ray diffraction. When the X-ray diffraction pattern of these organic thin films was examined with the diffractometer, it was found that diffraction lines were composed only of (00*l*) reflection and other reflections were missing completely (Fig. 4). This is the evidence for the fact that the crystallites of aromatic hydrocarbons were in alignment with their a·b planes parallel with the film surface. The mode of arrangement of crystallites is quite independent on the substrate materials which were described in the above section.

The electron microscopic observation and the application of electron microdiffraction verified the foregoing conclusion: From the electron micrographs (Fig. 5), it is found that the films consist of a number of single crystals which are arranged in closed packing with each other on the substrate, and the electron microdiffraction reveals that the crystallites are in alignment with their a·b planes parallel with the film surface.

Therefore, the discrepancy in resistivity between the surface-type and the sandwich-type cells could be attributed to the substantial anisotropy of resistivity of the crystals. Thus, the resistivity along the a·b plane of crystal should be much smaller than that perpendicular to the same plane for these compounds.

This conclusion is consistent with the results observed with anthracene single crystal. Mette and Pick have reported the anisotropy of electrical resistivity in anthracene⁶⁾, that is to say, the conductivity in a·b plane was a few times higher than that in a·c plane. Compton, Schneider and Waddington observed that the photocurrent along the b-axis direction is about one hundred times higher than that in the c-axis direction and several times larger than that along the a-axis direction⁷⁾.

The a·b plane is the cleavage plane of the crystal, and the molecules are so arranged that the molecular planes are nearly perpendicular to this plane. The nearest approach of neighboring molecules is found in the a·b plane. If there could be overlapping of molecular orbitals of π-electrons between neighboring molecules, it should take place along the direction parallel to this a·b plane. On the other hand, there is no reason to expect a stronger interaction between molecules in the direction along the c-axis. Therefore, it is reasonable to find the least value of resistivity along the a·b plane.

From Table I, it is seen that the anisotropy is found in the value of resistivity but not in the value of energy gap. Hence, there is no reason to expect a difference in the number of charge carriers which are in excited state. There should, however, be a large difference in the mobility of carriers depending on the direction of drift.

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6) H. Mett and H. Pick, *Z. Physik*, **134**, 566 (1953).

7) D. M. J. Compton, W. G. Schneider and T. C. Waddington, *J. Chem. Phys.*, **27**, 160 (1957).

Summary

It was found that the various types of conductivity cells of aromatic hydrocarbons possess great discrepancies of their electrical resistivity. The resistivity observed with the sandwich-type cell, perylene; $10^{18\sim19}\,\Omega$cm., coronene; $10^{17\sim18}\,\Omega$cm., and violanthrene; $10^{14}\,\Omega$cm., is in quite good agreement with that of the bulk specimen. However, a great difference was found between the resistivities of the sandwich-type and the surface-type cells, perylene; $10^{13}\,\Omega$cm., coronene; $10^{12\sim13}\,\Omega$cm., and violanthrene; $10^{9}\,\Omega$cm. This discrepancy in resistivity can be assumed to be introduced from the textured structure of the evaporated films and the substantial anisotropy of crystals; the crystals are in alignment with their a·b plane with the film surface. This orientation was found from the X-ray diffraction results, combined with the electron microscopic observation and the electron microdiffraction results.

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