Semi- and Photo-conductivity of Molecular Single Crystals. Anthracene and Pyrene

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Introduction

Recent works[1,2] in our laboratory have shown that some of the polycyclic aromatic compounds have fairly good electrical conductivity and sensitive photoconductivity in the solid state. From those and the other related properties, such as ultra-violet luminescence and xerographic phenomena, they are considered to be organic semi-conductors[3].

Since the preparation of single crystals of these compounds is generally very difficult, the measurements of electrical resistivity have been made hitherto for specimens in powdered form. In such a condition, the resistivity depends upon the compressive pressure; that is, it decreases remarkably with increasing pressure up to 80 kg./cm², however, thereafter it becomes approximately constant. Therefore in the preceding reports the electrical resistances of these organic semi-conductors were determined under compression beyond 80 kg./cm²*.

However, it is to be hoped that some single crystal could be obtained and the semi-conductivity would be measured in the single crystal state. It is difficult to obtain single crystals of compounds with larger molecular weight of this series, but in the case of smaller compounds, it is frequently possible to obtain single crystals of large size.

In this paper, the photo- and semi-conductivity of anthracene and pyrene in the single crystal state are presented.
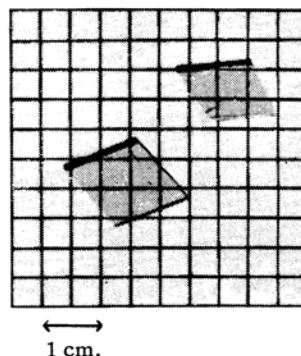

←——→
1 cm.

Fig. 1. Single crystals of pyrene.

Specimens

Since anthracene, a technical production from coal-tar, includes tetracene and carbazol, and the purification from these impurities is very difficult, pure anthracene was synthesized from anthraquinone by reduction*. This specimen was made of colourless plates, which melted at 219°C, and possessed a blue-violet luminescence. On the other hand, pyrene was recrystallized several times from aromatic solvent, and finally sublimed in a vacuum. Purified pyrene melted at 148°C, and possessed a whitish yellow colour.

Large single crystals (12 mm. × 10 mm. × 1 mm. rhomb.) of those could be grown by slow evaporation of solvent over a month in Solvesso (Standard Vac. Oil Co.). The beautiful plate-shaped single crystal obtained here was extended along [110] as shown in Fig. 1 (pyrene).

Experimental Procedure

Measurements of the electrical conductivity and the photoconductivity were made in the following manner as shown in Fig. 2. A sandwich type cell was made by coating one plane of the crystal (3) with an aluminium film (1) and the inversed plane with a half-transparent aluminium film (2).

1) H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, 18, 810 (1950), 20, 1481 (1952).

2) H. Inokuchi, This Bulletin, 24, 222 (1951); 25, 28 (1952), 27, 22 (1954).

3) H. Akamatu, "Organic Semi-conductors", Iwanami, Kagaku (1954), 282.

* The effect of hydrostatic pressure up to 8,000 kg./cm² on the semiconductivity of isoviolanthrone was reported in this Bulletin, 28, 570 (1955).

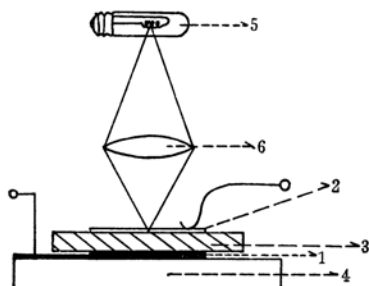* This anthracene was synthesized by Mr. J. Aoki in our laboratory.

Fig. 2.   The apparatus for measuring the semi- and photoconductivity.

This cell was mounted on a polystyrene plate (4), which was held in a box to control the temperature of the crystal, and it was supplied with a field of up to 11,000 volt per cm.

The electrical conductivity was measured perpendicular to the [110] plane of crystal by the potential drop method with the aid of a direct current amplifier. The light source, illuminating the crystal, was a tungsten or mercury vapour lamp (5), and a beam of light was directed on the specimen by means of a quartz lens (6).

Results and Discussion

Since the electrical resistivity of these single crystals was fairly high at room temperature, the measurements of resistance were made at the range from 50° to 150°C. Above this temperature the crystals were broken by sublimation.

The observed relation between electrical current and potential of anthracene is shown in Fig. 3.   Below 2,000 volt per cm. this curve obeyed Ohm's law approximately, but above 5,000 volt per cm. employed on the crystal heated at 136°C, this linearity was highly deviated, and at 152°C when the potential was applied to 7,500 volt per cm., the current had a very large value as shown in this figure.   Within this range of voltage employed here, the potential-current relation was reproducible.   Then it is reasonable to assume as follows: In such a high electric field, there will be a few electrons which can gain energy from the field and remove
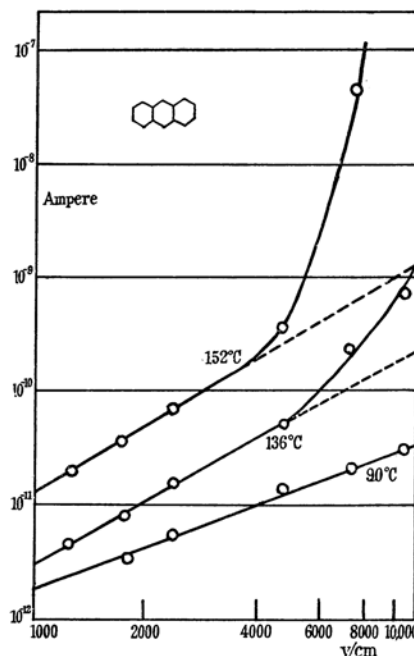

Fig. 3.   The relation between electrical current and potential for anthracene.

themselves from the occupied band. The number of free electrons and hence the current will increase rapidly; i. e., this phenomenon is the preceding one of the dielectric break-down[4].

The electrical resistivity and its temperature dependency of anthracene and pyrene were measured at the applied field of 1,000 volt per cm.   The temperature (T) dependency of electrical resistivity (ρ) has been expressed by the following formula,

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

where k is the Boltzmann constant and $\Delta\varepsilon$ is the activation energy.   The observed values of those are tabulated on Table I and are shown in Fig. 4.

To study the correlation between the thermal activation energy and the absorption spectrum of crystal, the author has measured

TABLE I

THE VALUE OF ρ_0, $\rho_{\text{at 15°C}}$, $\Delta\varepsilon$ AND ENERGY GAP FROM ABSORPTION SPECTRA OF ANTHRACENE AND PYRENE

	ρ_0	$\rho_{\text{at 15°C}}$	$\Delta\varepsilon$	Energy gap from absorption spectra
Anthracene	$1 \times 10^{-2} \Omega$ cm.	$10^{22} \Omega$ cm.	2.7 eV.	3.0 eV.
	$5 \times 10^{-1} \Omega$ cm.[1]	$10^{17} \Omega$ cm.[1]	1.65 eV.[1]	
Pyrene	$1 \times 10^{-3} \Omega$ cm.	$10^{20} \Omega$ cm.	2.4 eV.	2.8 eV.

1) from H. Mette and H. Pick[5].

4) N.F. Mott and R.W. Gurney, "Electronic Processes in Ionic Crystals", Oxford Univ. Press, 2nd ed. (1948), p. 197.
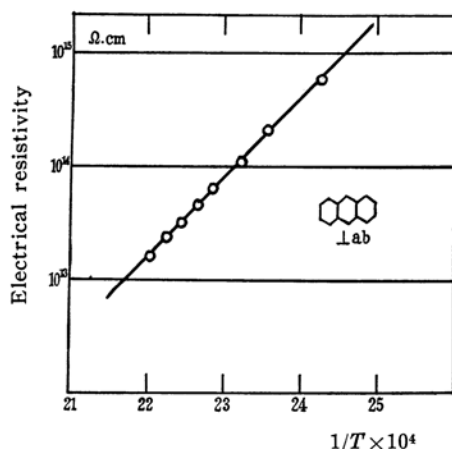
Fig. 4a.   The relation between resistivity
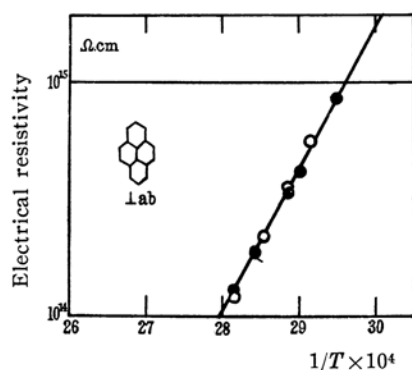and temperature for anthracene.

Fig. 4b.   The relation between resistivity
and temperature for pyrene.

the absorption spectrum of a single crystal
(perpendicular to [110] plane of crystal). The
longest wave edges of the absorption spectra
are shown in Table I. This value and the
thermal activation energy ($\Delta\varepsilon$) coincided with
each other; then this will be due to the fact
that molecular single crystals are intrinsic
semi-conductors as in the case of the pow-
dered form.

H. Pick and H. Mette[5] (University of Göt-
tingen) have reported, however, that the
thermal activation energy of anthracene was
1.65 eV. (a half of the value measured from
the longest wave edges of absorption spectra)
and their results on electrical resistivity was
too small as compared with my results. But
the same author has described in his next
article[6] on the electrical resistivity of naph-
thalene single crystal, that the energy gap
(3.7 eV.) observed from the temperature
dependency of electrical resistivity coincided
with the value of the longest wave edges of
absorption spectra (3,250 Å $\approx$ 3.86 eV.). It
seems to the present author that his speci-
men was not completely pure since his an-

thracene was purified from a crude one.

The photoconductivity of these single crys-
tals was detectable, and its potential depen-
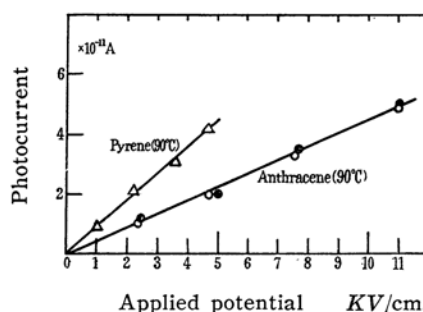dence was as shown in Fig. 5. These results

Fig. 5.   Photoelectric   current   plotted
against the voltages for single crystals.

show that the photocurrent in the single
crystal is a primary current as in the case
of other polycyclic aromatic compounds. It
was reported that the photoconductive pro-
cess in the conjugated organic compounds
in powdered form is enhanced by the oxygen
in the air[7,8], but my results showed that
the photocurrent was not enhanced by the
oxygen in the air as illustrated in Fig. 5.
In this figure the points denoted as ○ show
the photocurrent-voltage characteristics in
the vacuum (10^{-2} mmHg) and ● the same
characteristics in the air.

Summary

The electrical resistivity and photoconduc-
tivity of single crystals—anthracene and
pyrene—, which could be grown by slow
evaporation of a solvent over a month
in Solvesso, were measured. The tempera-
ture dependency of electrical resistivity (ρ)
has been expressed by the next formula,
$\rho = \rho_0 \exp(\Delta\varepsilon/2kT)$, and the values of resisti-
vity ($\rho_{at\ 15°}$) and thermal activation energy
($\Delta\varepsilon$) are $10^{22}\Omega$ cm., 2.7 eV. for anthracene and
$10^{20}\Omega$ cm., 2.4 eV. for pyrene. This activa-
tion energy and the longest wave edges of
absorption spectra in the solid state coincided
with each other, then this phenomenon will
be due to the fact that molecular single
crystals are intrinsic semi-conductors as in
the case of powdered form.

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5) H. Mette and H. Pick, *Z. Physik*, **134**, 566 (1953).
6) H. Pick and G. Wissman, *Z. Physik*, **138**, 436
(1954).

7) A.G. Chynoweth and W.G. Schneider, *J. Chem.*
Phys., **22**, 1029 (1954).
8) A.T. Vartanyan, *Doklady Akad. Nauk, S.S.S.R.*,
71, 641 (1950).