Semiconductivity of Phenanthrene Single Crystals[*]

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Extensive studies have been made of the electrical properties of the anthracene single crystal,[1-4] which is now regarded as a model substance for the investigation of the semiconductive properties of aromatic hydrocarbons.

In order to elucidate the mechanism of electronic conduction in organic solids, it is also important to accumulate reliable data on the electrical properties of other relatively simple hydrocarbons. However, on phenanthrene, a structural isomer of anthracene, the available experimental results are quite limited.[5]

In the present work, the electrical conductivity and its anisotropy will be studied in detail on phenanthrene single crystals, and the results will be compared with the related behavior of anthracene.

Experimental

Material.—Powdered phenanthrene of a chemical-purpose grade obtained from the Eastman Kodak Company was purified by recrystallization from an ethanol solution, followed by vacuum sublimation. Each purification process was carefully repeated more than four times.

In the fluorescence spectrum of the resultant flaky and colorless sample, there was no peak other than those of phenanthrene reported in the literature,[6] except for a slight variation in the intensity. This variation may be due to the difference in the crystalline state.

Crystal Growth.—Crystals of purified phenanthrene with a melting point of 103°C were grown by means of a modified Bridgeman method.

In the electrical furnace applied here, the upper part was maintained at a temperature a little higher than the melting point of the sample, and the bottom part, at a temperature lower; there was a large temperature gradient, about 10°C/cm., in the middle part.

The powdered sample was sealed under a $10^{-3}\sim10^{-4}$ mmHg vacuum into a cylindrical glass tube, the bottom of which was sharpened like a pencil. The tube was lowered at the rate of $1\sim2$ mm. per hour through the center of the furnace.

In this process, the crystal grew its ab plane perpendicular to the isothermal plane in the furnace.

Crystals of about $8\times8\times15$ mm. could thus be made, but in most cases, cracks developed along the ab plane soon after the preparation. Therefore, only uncracked portions were cut out from them to use for the electrical measurement.

Specimen Cell.—An electrical conductivity cell of the sandwich type was prepared on a Teflon block, as is schematically shown in Fig. 1.

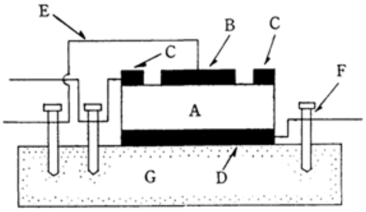

Fig. 1. The conductivity cell of sandwich type.

A: Crystal, B: Front electrode
C: Guard-ring electrode
D: Back electrode, E: Lead wire
F: Terminal, G: Teflon block

The cell had a guard-ring electrode which was grounded in order to prevent an effect of the surface current.

Silver paste (Ecco Bond), which was found to make ohmic contact with this sample, as will be described in the following paragraph, was applied as electrodes. The following two kinds of cells were used to measure the electrical resistivity in two crystallographic directions: the ⊥ab plane and the ∥ ab plane.

(1) The ⊥ab cell, the electrodes of which were painted on both sides of the ab plane of a crystal in order to evaluate the electrical resistivity perpendicular to this plane ($\rho_{\perp ab}$).

(2) The ∥ab cell, the electrodes of which were attached on both sides of the plane perpendicular to the ab plane in order to observe the electrical resistivity parallel to the ab plane ($\rho_{/\!/ ab}$).

Measurements.—The measuring apparatus consisted of a vibrating reed electrometer (Takeda TR-88).

The current-voltage characteristics were examined in an atmosphere of air and nitrogen gas in order to find the effect of an ambient atmosphere on the electrical conductivity of the sample. The measurement of the temperature dependence of the electrical resistivity was made over the temperature range

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from 24 to 75°C for both increasing and decreasing temperatures.

Results and Discussion

The current-voltage characteristics of the specimen ∥ab cell in air and in nitrogen gas at room temperature are shown in Fig. 2.

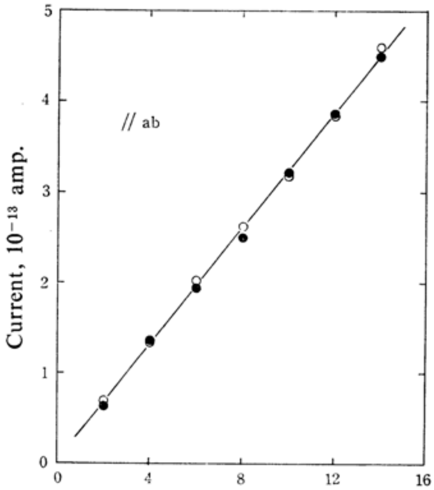

Fig. 2. The current-voltage characteristics of phenanthrene.
○ in air
● in nitrogen gas

There was no difference between the current in air and that in nitrogen gas within the range of experimental error. Therefore, the observation of the temperature dependence of the electrical resistivity was made in air.

As is exemplified by the same figure, the current-voltage relation was linear up to 1600 V. per cm. A similar result was obtained for the specimen ⊥ ab cell.

As has been reported in many papers on the semiconductive property of organic compounds, the observed temperature dependence of the electrical resistivity of phenanthrene is, for both increasing and decreasing temperatures, in good agreement with the following expression, as is shown in Fig. 3.

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

where ρ is the electrical resistivity, $\varDelta\varepsilon$ is the thermal activation energy, k is the Boltzmann constant, and T is the abolute temperature. The values of $\varDelta\varepsilon$, ρ_0, and the resistivity at 15°C, ρ_{15}, are given in Table I. The last value was estimated by extrapolation from the observed temperature dependence.

There is no anisotropy in the value of the activation energy. An anisotropy can be found, however, in the value of the electrical resistivity; the electrical resistivity measured on the ab plane ($\rho_{/\!/ab}$) is lower by a factor of about twenty-five than that perpendicular to this plane ($\sigma_{\perp ab}$).

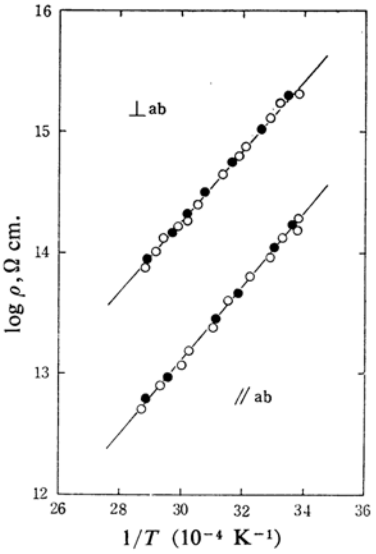

Fig. 3. The temperature dependance of the resistivity of phenanthrene.
○ for increasing temperature
● for decreasing temperature

TABLE I. THE ELECTRICAL RESISTIVITY OF PHENANTHRENE OBSERVED FROM ⊥ab CELL AND ∥ab CELL

	ρ_{15}, Ω cm.	$\varDelta\varepsilon$, eV.	ρ_0, Ω cm.
Phenanthrene			
⊥ab	4.8×10^{15}	1.14	5.5×10^{5}
∥ab	1.9×10^{14}	1.15	1.8×10^{4}
powder*	1.4×10^{16}	1.3	6×10^{4}
Anthracene			
⊥ab**	10^{22}	2.7	1×10^{-2}
powder*	1.7×10^{20}	2.47	4×10^{-2}

* From J. B. Rust et al.
** From H. Inokuchi et al.

The electrical conductivity (σ) can be expressed as $\rho=|e|n\mu$, where n is the concentration of the charge carrier and μ, the mobility of the carrier.

Since no anisotropy is found in the activation energy, it is not likely that the concentration of the charge carrier varies according to the direction of the electric field. Therefore, it seems that the observed anisotropy in the electrical conductivity results from the difference in the mobility of the charge carrier. This assumption has been affirmed by the mobility anisotropy in anthracene obtained through a pulsed photoconductivity technique³⁾ and tight-binding band calculations.⁴⁾

The conductivity anisotropy observed with a phenanthrene crystal is, however, larger than that of anthracene reported by Mette and Pick,[1] who have found that in the anthracene crystal, the conductivity on the ab plane is a few times higher than that in the direction perpendicular to the plane. Such a difference might be due to the difference in the band structures between phenanthrene and anthracene.

As the molecules in a phenanthrene crystal are arranged so that the molecular planes are nearly perpendicular to the ab plane,[7,8] the overlapping of π-orbitals are largest in the direction parallel to the ab plane. The resistivity is lowest in this direction, as has been found to be true in anthracene[1] and other substances.[9]

There is an appreciable difference between phenanthrene and anthracence in the absolute values of $\Delta\varepsilon$ and ρ_{15}, as is shown in Table I. A similar result has been reported also by Rust et al. as a result of their experiment with powder specimens.[5]

Therefore, we must conclude that while phenanthrene and antheacene are structural isomers and have similar crystallographic characters,[7,8,10] the electrical properties of the two substances are markedly different.

Summary

Phenanthrene single crystals have been grown by means of a modified Bridgeman method. The electrical conductivity has been measured for two crystallographic directions, ⊥ ab and ∥ab.

The electrical resistivity is not affected appreciably by ambient oxygen. The temperature dependence of electrical resistivity can be described as $\rho=\rho_0 \exp(\Delta\varepsilon/2kT)$, where the activation energy ($\Delta\varepsilon$) is 1.14 eV. for ⊥ab and 1.15 eV. for ∥ ab; the two values agree well. A large anisotropy has been found in the resistivity at 15°C. The resistivity is 4.8×10^{15} Ω cm. and 1.9×10^{14} Ω cm. for ⊥ ab and ∥ab respectively.

It has been concluded that, although phenanthrene is an isomer of anthracene, the electrical properties of phenanthrene differ considerably from those of anthracene.

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