Semiconductivity and Absorption Spectrum of Perylene Single Crystal

By Mizuka SANO and Hideo AKAMATU

(Received March 6, 1961)

Concerning the electronic conduction in organic solids, most of which are aromatic compounds, the investigation on single crystals is of special interest. For instance, it is desirable to determine the anisotropy of the electrical conductivity. If it is presumed that the conduction takes place in association with the overlapping of π-electron orbitals, the resistivity should be the lowest in such a direction where the overlapping is the largest. Mette and Pick(1) have observed such an anisotropy in the anthracene single crystal. We have found a similar anisotropy of thin evaporated films of perylene, coronene and violanthrene in which minute crystals are in alignment along the textured structure(2). In this note, the investigation on the perylene single crystal is presented. It contributes to the above argument and suggests the correlation between the conduction level and the electronic absorption band in the molecular crystal.

Perylene, which was synthetized from naphthalene following Scholl(3), was recrystallized from the benzene solution and the gracial acetic acid solution successively, then sublimed in vacuo. However, these procedures could not

---

1) H. Mette and H. Pick, *Z. Phys.*, **134**, 566 (1953).

2) H. Inokuchi, H. Kuroda and H. Akamatu, This Bulletin, **34**, 749 (1961).

3) R. Scholl, *Ber.*, **43**, 2202 (1910).

eliminate a trace of reddish substance, terrylene ($C_{30}H_{16}$). Finally, the chromatographic technique with alumina was applied to its benzene solution in the dark. Subsequent sublimation yielded a faint yellow product.

Thin perfect single crystals were obtained when the sublimation procedure was carefully controlled and made to be slow. In a favorable condition, flake-like crystals were produced on the glass wall, which possessed the area of about $4\times6\,\text{mm}^2$ with the thickness of 60~280 μ. It was proved by means of the X-ray diffraction that the surface plane of the flake-like crystal is the (001) plane.

The electrical resistivity was measured by applying the voltage perpendicularly to the (001) plane, or in parallel to the plane. Aquadag was employed as the electrodes. The voltage source was a battery of dry elements with a voltage up to 450 V. The measurement was carried out, with the aid of direct current amplifier, in vacuo (10^{-3} mmHg) over a temperature range from 40 to 110°C.

No departure from Ohm's law was observed in the voltage region employed (up to 1.6×10^3 V./cm.). The resistivity decreased with increasing temperature and a good linear realationship was obtained between the logarithm of the resistivity (ρ) and the reciprocal of the temperature, (Fig. 1), which indicates the applicability of the following formula.

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

where ε is the energy gap.

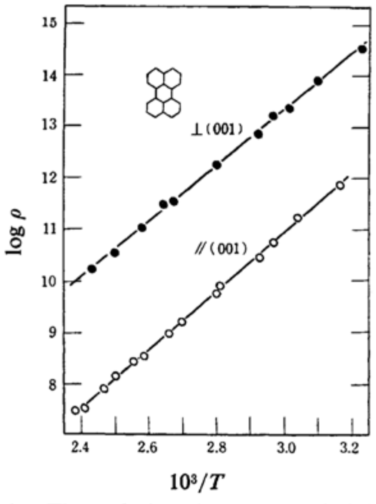

Fig. 1. The relation between resistivity and temperature for perylene single crystal.

It was found that the resistivity is isotropic in the (001) plane. But in the direction perpendicular to this plane, the resistivity is higher by a factor of 10^2 than that in the (001) plane, (Table I).

TABLE I. THE VALUES OF ε AND $\rho_{15^\circ\text{C}}$ AND THE ABSORPTION SPECTRUM OF PERYLENE CRYSTAL

	ε eV.	$\rho_{15^\circ\text{C}}$ Ω·cm.
⊥ (001)	2.1	6.5×10^{15}
∥ (001)	2.2	4.1×10^{13}
Film*		
from the sandwich-type cell	2.0	$10^{18}\sim10^{19}$
from the surface-type cell	2.2	10^{13}
Absorption spectrum		
the peak of the *p*-band	2.67	
the onset of the *p*-band	2.26	

* after Inokuchi, Kuroda and Akamatu²⁾

The absorption spectra of the perylene crystal and its solution in ethyl alcohol were recorded by the spectrophotometer (Cary model 11). The spectrum of the single crystal resembles closely that of the solution, excepting some broadening and a small shift toward the long wavelength side. In consequence, according to Clar's classification⁴⁾, the absorption bands of the crystal can be assigned to the *p*-, α- and β-band respectively, referring to the absorption bands of the solution.

In the neighborhood of the absorption edge, it is rather difficult to decide precisely the threshold value. However, the onset of the *p*-band is found in the vicinity of 466 mμ for the solution and 550 mμ for the crystal. The value of light quantum for the latter is in agreement with the observed value of ε, (Table I).

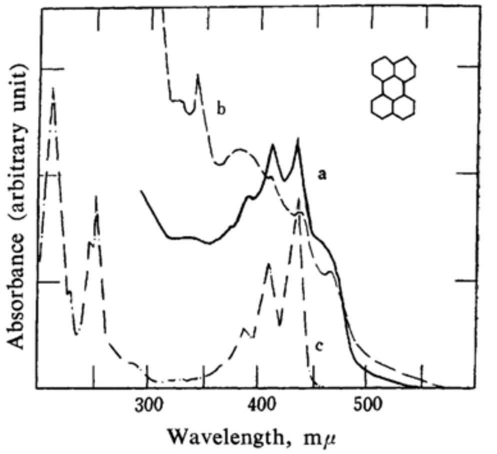

Fig. 2. Absorption spectra of perylene. (a) Single crystal, (b) Evaporated film, (c) Solution in ethyl alcohol

The anisotropy was found in regard to the conductivity, but not to the value of the energy gap. The same result has been obtained for

---

4) E. Clar, "Aromatische Kohlenwasserstoffe", Springer Verlag, Berlin (1952).

the evaporated film of perylene[2]. It can be concluded that the anisotropy arises due to the difference in the mobility of free carriers which is dependent on the direction of drift, but not due to the difference in the number of carriers which are in thermal equilibrium.

The direction of π-bond orbitals in each molecule extends perpendicularly from the molecular plane, and molecules are arranged in the crystal in such a way that the molecular planes are parallel with each other with a distance of 3.47 Å and nearly perpendicular to the (001) plane[5]. Therefore, the direction of the lowest resistivity is coincident with the direction of the extending of π-bond orbitals of molecules in the crystal. The maximum overlapping of the orbitals is expected to be between neighboring molecules in this direction.

If a conduction level could be assumed in the molecular crystal, the observed value of the energy gap implies that it lies in the neighborhood of the onset of the p-absorption band. No theory has yet explained the reason why the lowest excited state contributes to the conduction, but it is likely that the excitation of π-electrons to the lowest excited singlet state is the first process of electronic conduction in the perylene crystal.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo

---

[5] D. M. Donaldson, J. M. Robertson and J. G. White, *Proc. Roy. Soc.*, **A220**, 311 (1953).