

Photoconductivity of the Condensed Polynuclear Aromatic Compounds

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Introduction

In previous works, H. Akamatu and the present author have reported that violanthrone, isoviolanthrone and pyranthrone have photoconductivity and intrinsic semi-conductive characters.^{1,2)} Similar behaviour was found for the other related compounds, that is, the condensed polynuclear aromatic and aza-aromatic compounds.^{3,4)} For example, indanthrone black ($C_{34}H_{14}N_2O_2$) has the electrical resistivity of $2.5 \times 10^8 \Omega\text{cm}$. and ovalene ($C_{32}H_{14}$) has $2.3 \times 10^{15} \Omega\text{cm}$. Such particular pure compounds as these have never been found as shown in Fig. 1 in measurements of the electrical conductivity of many sorts of compounds. And also, this group of compounds shows luminescent character by the actions of cathode-ray and ultra-violet light in the solid state.⁵⁾ These characters will be attributed to the intermolecular overlappings of the electron clouds of π -electrons in the polynuclear condensed aromatic rings.

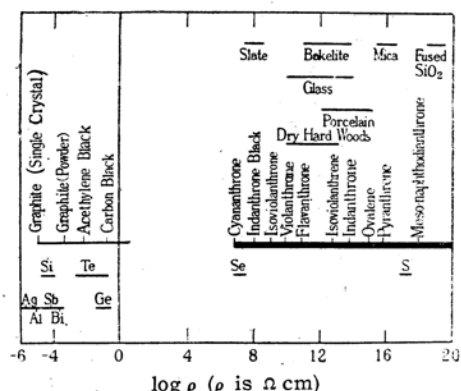


Fig. 1. The electrical resistivity diagram of substances.

Up to the present, the researches of semi-conductors have been mostly restricted to the field of inorganic substances, thus these compounds occupy a new field in the branch of semi-conductive materials. We may call

these organic compounds—*organic semi-conductors*.

Experimental Procedure

In these compounds, the photoconductivity of isoviolanthrone, violanthrone, isoviolanthrene, violanthrene, pyranthrone, pyranthrene, ovalene, flavanthrone, indanthrone and indanthrazine was measured. These materials have been purified chemically by the usual methods, and then sublimed *in vacuo* more than twice until the electrical conductivity became constant^{3,4,6)}.

Excepts for violanthrone and isoviolanthrone, a photocell was made following the so-called "sandwich" type as illustrated in Fig. 2. The cells were formed by evaporating organic semi-conductors (1)* on a quartz plate (dimension is $1\text{mm} \times 10\text{mm} \times 50\text{mm}$) (2) which had been previously coated with a transparent aluminum conducting film (3). The second electrode (4) could be made by depositing a thin layer of aluminum by evaporation on the surface of the film of the organic substances. Further, both sides of this plate were painted with colloidal graphite (5), (6) as electrical terminals. Further details are shown in Fig. 2.

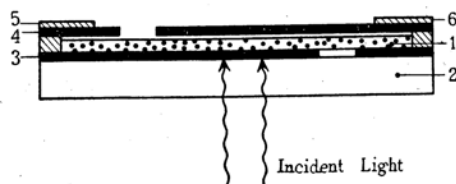


Fig. 2. "Sandwich" type photocell for photoconductivity measurements. (1) photoconductive organic semi-conductor, (2) quartz plate, (3) transparent aluminum electrical conducting film, (4) thin layer of aluminum as a second electrode, (5) & (6) colloidal graphite electrodes as electrical terminals.

For violanthrone and isoviolanthrone, the film of these compounds was deposited by vacuum evaporation between tin foils, 10mm in width, which were stuck on a quartz plate, keeping the gap between them 1 mm.

The photoelectric current of the cells was produced by illumination of monochromatized light

1) H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **20**, 1431 (1952).

2) H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950).

3) H. Inokuchi, *This Bulletin*, **24**, 222 (1951).

4) H. Inokuchi, *This Bulletin*, **25**, 23 (1952).

5) H. Akamatu, unpublished.

6) H. Akamatu and K. Nagamatsu, *J. Colloid Sci.*, **2**, 593 (1948).

* For example, violanthrene are sublimed, at $300^\circ\text{--}350^\circ$, at 10^{-4}mm.Hg and pyranthrene, at $250^\circ\text{--}300^\circ$, at 10^{-4}mm.Hg . Heats of sublimation of those are $52.3 \pm 2.1\text{ kcal. mol.}$ and $45.3 \pm 1.6\text{ kcal. mol.}$ respectively. Details of this problem were reported in this Bulletin, **25**, 299 (1952). H. Inokuchi, S. Siba, T. Handa and H. This Bulletin, **26**, 364 (1953).

from a 500 watts tungsten lamp, operating at a constant voltage of 75 volts.

These condensed aromatic compounds are typical molecular crystals and have no impurities, that is, they are intrinsic semi-conductors. Therefore, their physical properties don't change by further steps of sublimation. This character is very advantageous for the measurement of photoconductivity compared with inorganic semi-conductors, such as Sb_2S_3 and CdS .

The optical absorption of solid state was observed by the LiF monochrometer. In this experiment, the organic substances were evaporated on a quartz plate or a glass one, as a thin layer, which had from 10 to 100 micron thickness.

Results and Discussions

Gudden and Pohl have described in their famous works⁷⁾, that a photoelectric current is separated into two types, viz., primary current and secondary current. The former is a motion of charges, electrons and holes, released throughout the illuminated volume by the action of photoelectrons and the latter is introduced with the contribution of the lowering of electronic barriers by the primary current, thus permitting the flow of additional electrons.

The photoelectric current observed here is proportional to the intensity of the incident light as shown in Fig. 3. This character is one of the most distinct properties of a primary current. Then, it may be reasonable to say that the observed photocurrent in this experiment is a primary current.

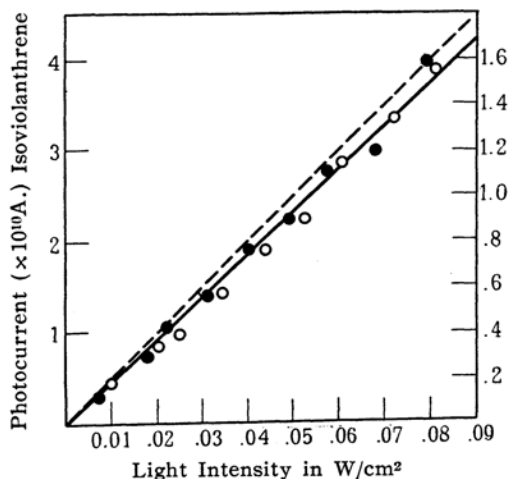


Fig. 3. Photoelectric current as a function of the intensity of illumination for ovalene photocell (—○—○—) and isoviolanthrene photocell (—●—●—) at 270 V. potential difference across these layers.

When "isoviolanthrene photocell" was illuminated by the white light (0.055 W./cm^2),

the photoelectric current of this cell was changed with applied potential across the isoviolanthrene layer as shown in Fig. 4. When the thickness of film was from 50 up to 100 micron, then a 10^3 V. potential difference across the layer corresponded to 10^4 V./cm. This character was similar to the amorphous selenium film⁸⁾. The photoelectric current increased nearly linearly with applied voltage and didn't indicate any saturation

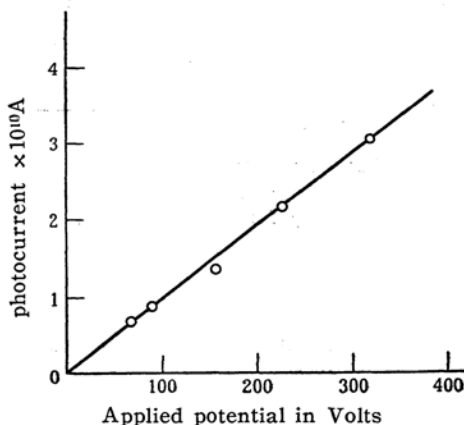


Fig. 4. Photoelectric current plotted against the Voltages applied across the isoviolanthrene photocell for the illumination of the white light (0.055 W./cm^2).

at the possible high voltage (270 V.). The ordinary semi-conductors, such as ZnS , have a saturated photocurrent at 10^3 V./cm^2 .

The photocells of ten organic substances, described already, were made and the photoelectric current at 270 V. potential difference across these organic semi-conductive layers, which was illuminated at 10^{-3} – 10^{-4} W./cm^2 intensity monochromatized light, was measured. The spectral response of photoelectric current is shown in Fig. 5-7.

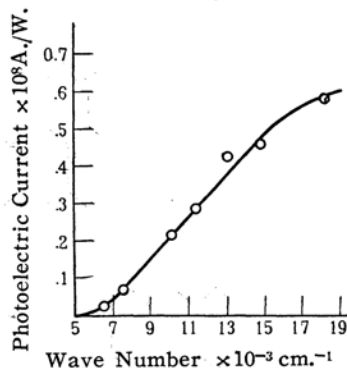


Fig. 5. Spectral response of photoconductivity for the flavanthrone photocell.

7) B. Gudden, "Lichtelektrische Erscheinungen," Julius Springer, Berlin, 1928.

8) P. K. Weimer and A. D. Cope, *R. C. A. Rev.*, **12**, 314 (1951).

9) B. Gudden and R. Pohl, *Z. f. Phys.*, **17**, 331 (1923).

The photocurrent decreased as the wavelength of the incident light increased in each case, and the threshold was found. The

value of light quantum in e.V. at each threshold is illustrated in TABLE I.

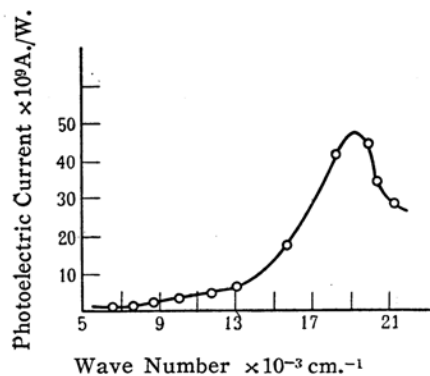


Fig. 6. Spectral response of photoconductivity for the isoviolanthrene photocell.

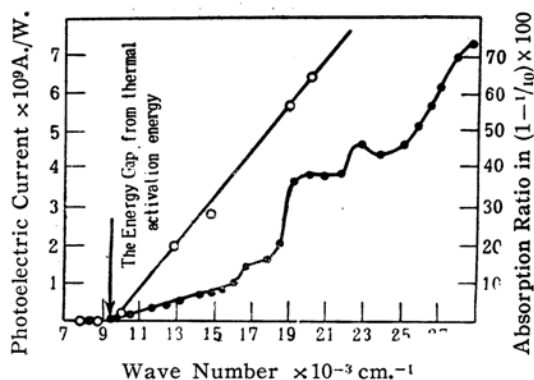
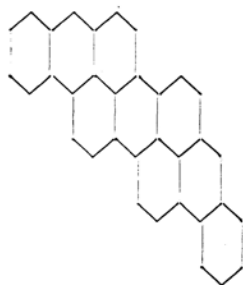


Fig. 7. Spectral response of photoconductivity and optical absorption curve for ovalene —○—○—○— photoconductive response, —●—●—●— optical absorption curve.

TABLE I. THE ENERGY GAP OF THE CONDENSED POLYNUCLEAR AROMATIC AND AZA-AROMATIC COMPOUNDS

Substance	Structure	Energy gap in e.V. unit		
		from photoconductivity	from optical absorption	from thermal activation energy
Isoviolanthrone		0.93	0.7—0.7 ₅	0.75
Violanthrone		0.84	0.7 ₅	0.78
Isoviolanthrene		0.85	—	0.82

Violanthrene



0.88

0.8

0.85

Ovalene

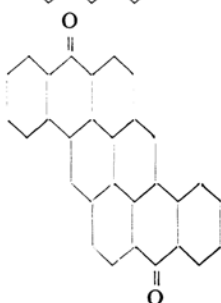


1.20

1.2

1.13

Pyranthrone

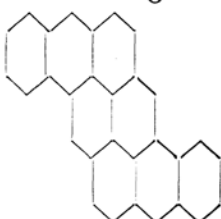


1.14

0.8—0.8₅

1.06

Pyranthrene

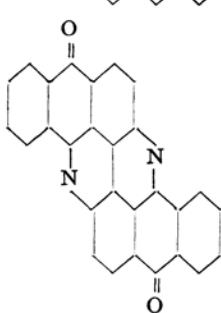


0.85

0.7₅—0.8

1.07

Flavanthrone

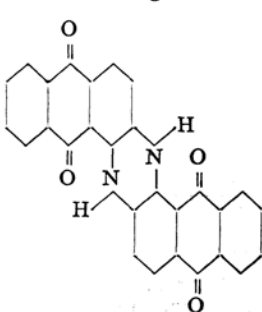


0.76

0.7—0.7₅

0.70

Indanthrone

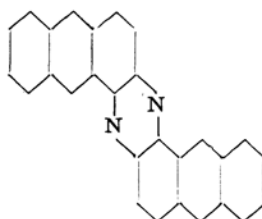


0.74

0.6₅

0.63

Indanthrazine



0.80

0.65—0.7

0.66

The observed dark currents were changed with substances measured, with thickness of films and with other conditions. However, when the photocell was illuminated with the tungsten lamp, which had 0.1 W/cm^2 intensity, the ratio of photocurrent to dark current was about from 5 to 20 times. For

example, the photocurrent and dark current of indanthrone were $5.14 \times 10^{-11} \text{ A}$ and $1.37 \times 10^{-11} \text{ A}$, pyranthrone $19.6 \times 10^{-11} \text{ A}$ and $2.7 \times 10^{-11} \text{ A}$ and this ratio of "ovalene photocell" was very large, such as $140 \times 10^{-10} \text{ A}$ of photoelectric current and $1.54 \times 10^{-10} \text{ A}$ of dark current at room temperature. This is very

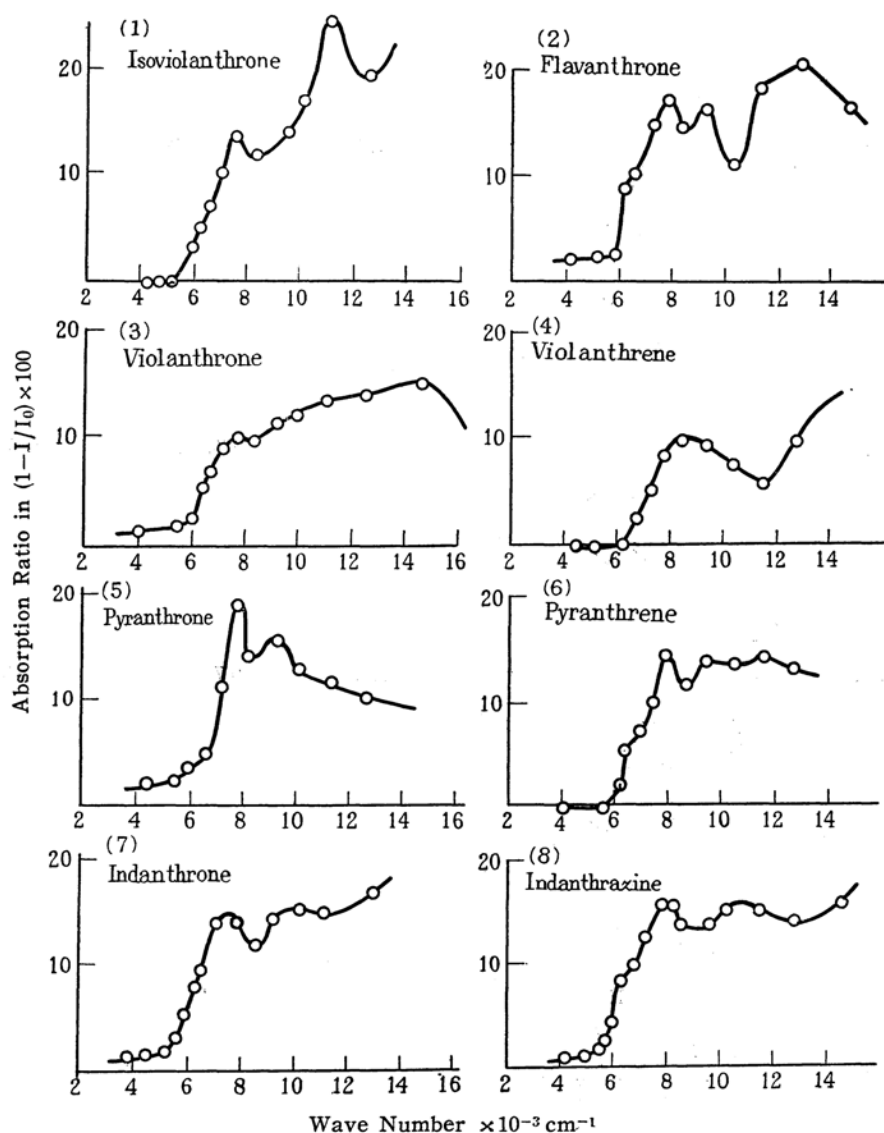


Fig. 8. Optical absorption of the organic semi-conductors. (1) isoviolanthrone, (2) flavanthrone, (3) violanthrone, (4) violanthrene, (5) pyranthrone, (6) pyranthrene, (7) indanthrone and (8) indanthrazine.

interesting when compared with the molecular structure.

These organic semi-conductors have no impurities—intrinsic semi-conductors. Then, assuming a crystal band structure, the threshold values correspond to the energy gap between the full band and the empty band.

To study the correlation between the photoconductivity and the optical absorption of crystals, the author has measured the absorption spectrum of layers of these organic substances. The spectral response of this character is shown in Fig. 8, and the threshold values are tabulated in TABLE I in e. V. unit. In TABLE I, results of photoconductivity, the optical absorption of solid and the temperature dependence of electrical conductivity satisfactorily coincide with each other. For example, these three characteristics of ovalene are shown in Fig. 7.

This will be due to the fact that the organic semi-conductors studied here are intrinsic ones having molecular lattice.

Summary

Photoconductivity and optical absorption in the solid state of the organic semi-conductors, that is, isoviolanthrone (I), violanthrone (II), isoviolanthrene (III), violanthrene (IV), pyranthrone (V), pyranthrene (VI), ovalene (VII), flavanthrone (VIII), indanthrone (IX) and indanthrazine (X) were measured.

From the threshold values of the spectral response of the photoelectric current and optical absorption in the solid state, the energy gap between the full band and the empty band were estimated as (I) 0.93 eV, 0.7 eV, (II) 0.84 eV, 0.75 eV, (III) 0.85 eV, —, (IV) 0.88 eV, 0.8 eV, (V) 1.14 eV, 0.85 eV, (VI) 0.85 eV, 0.8 eV, (VII) 1.20 eV, 1.2 eV, (VIII) 0.76 eV, 0.75 eV, (IX) 0.74 eV, 0.65 eV, (X) 0.80 eV, 0.7 eV respectively. Also from the experimental facts that the photocurrent is proportional to the applied potential and to the light intensity, the author thinks that the photocurrent observed here is a primary current. These results, photoconductivity and absorption spectra, are in good agreement with that estimated from the temperature dependence of the electrical resistivity. It may be reasonable that this agreement is due to the fact that the organic semi-conductors studied here are intrinsic ones having molecular lattice.

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