# *Electric Properties of the Single-crystal and Thin Film of $\alpha$, $\alpha'$-Diphenyl-$\beta$-picrylhydrazyl*

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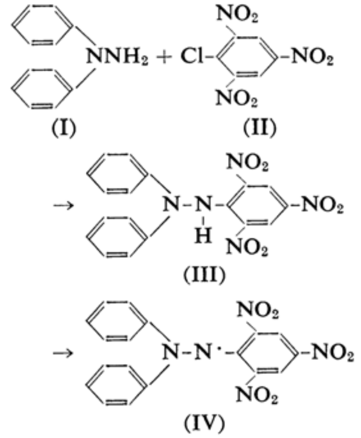
It is known that $\alpha,\alpha'$-diphenyl-$\beta$-picrylhydrazyl (DPPH) has one unpaired electron. The magnetic properties of the stable free radical have been studied by a number of investigators[1-4]. The unpaired electron localized on the nitrogen atoms of the molecule converts para-hydrogen into ortho-hydrogen at low temperature[5]. The conversion mechanism is a paramagnetic (physical) one, as absence of the hydrogen-deuterium exchange reaction rules out a dissociative chemisorption of hydrogen molecules by the free valencies of surface.

The works on the role of the unpaired electron in the interaction between free radicals and adsorbed oxygen or complexed organic solvents have been reported[6,7]. These results expressed that no change of the concentration of unpaired electrons is found with this interaction.

However, few articles concerning the electronic properties for solid free radicals have been published[5,8]. In this paper, we are presenting the electronic conduction and its related phenomena of the single crystal and the thin film of $\alpha,\alpha'$-diphenyl-$\beta$-picrylhydrazyl. Further, the relation between the orientation of molecules in the crystal and the electronic conduction will be discussed.

## Experimental Procedures

$\alpha,\alpha'$-Diphenyl-$\beta$-picrylhydrazyl was prepared by reaction of $\alpha,\alpha'$-diphenylhydrazine (I) with picryl chloride (II) in chloroform. The strong heating of this solution yielded precipitates of white crystallites, diphenylhydrazine hydrochloride. After separation of these precipitates from the solution, the addition of ether caused beautiful scarlet-red crystal, $\alpha,\alpha'$-diphenyl-$\beta$-picrylhydrazine (III), to precipitate. After the method of Goldschmidt and Renn[9], the oxidation of hydrazine with lead dioxide and anhydrous sodium sulphate, produced the violet crystal, $\alpha,\alpha'$-diphenyl-$\beta$-picrylhydrazyl (IV).



The solvent-free single crystal (dimension: $0.3\times0.3\times1.3$ mm., weight: about 1 mg.) of the free radical was grown from the carbon disulphide solution. Two types of thin film cells of DPPH were prepared by a vacuum evaporation as described in the previous report[10]. This evaporation had to be operated rapidly at a vacuum of the order of $10^{-5}\sim10^{-6}$ mmHg to avoid the decomposition of the free radical in specimen vessel under heating (80~130°C). The decomposition of the prepared thin free radical film was also accelerated by a contact with air and/or by an illumination of ultraviolet light. Therefore, the observation of its physicochemical properties was carried out in short period (one or two days) after preparation.

The semi- and photo-conductivities of the DPPH

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specimen were measured with an aid of vibration-reed electrometer. During the measurement, the specimen was kept in a vacuum vessel. The absorption spectra of the free radical were observed with a Cary recording spectrophotometer, model-14.

## Results and Discussion

The electrical resistivity*, $\rho$, and its activation energy of the DPPH single crystal were fairly high in comparison with the previous results[5,8]. It was found that a great anisotropy of these values occurs in the direction of the crystal: The conductivity along the long axis (c-axis) of needle crystal is higher than that perpendicular to the axis by a factor of $10^5$ as listed in Table I.

From a preliminary results, the crystal structure of DPPH is orthorhombic one, with four molecules in a unit cell of dimensions a = 17.6 Å, b = 18.9 Å and c = 7.59 Å and molecules in the crystal seem to be arranged perpendicular to the c-axis and the molecular planes are parallel with each other. The unpaired electron in the molecule is localized on the nitrogen atoms and the direction of its orbitals extends perpendicularly from the molecular plane as shown in Fig. 1. Therefore, the overlapping of the orbitals is expected to be large in the direction perpendicular to the molecular plane, but not in the parallel one to the plane. Since charge carriers in the free radical transfer through the overlapping, the anisotropy of conductivity might be a consequence of substantial anisotropy of the overlapping in the crystal.

As is illustrated in Table I, no direction dependency was found in the values of energy

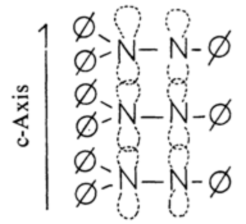

Fig. 1. The arrangement of DPPH molecules in crystal.

TABLE I. THE ELECTRONIC CONDUCTION IN DPPH

| Sample | Single crystal | | Thin film | |
|---|---|---|---|---|
| Direction | c-Axis ∥ | c-Axis ⊥ | Sandwich type | Surface type |
| $\rho_{15}$ | $1\times10^{10}$ Ω cm. | $1\times10^{15}$ Ω cm. | $\sim10^{13}$ Ω cm. | $\sim10^{10}$ Ω cm. |
| $\Delta\varepsilon$ | 1.5 eV. | 1.6 eV. | 2.7 eV. | 1.7 eV. |
| $\rho_0$ | $10^{-3}$ Ω cm. | $10^{2}$ Ω cm. | $10^{-4}$ Ω cm. | $10^{-2}$ Ω cm. |

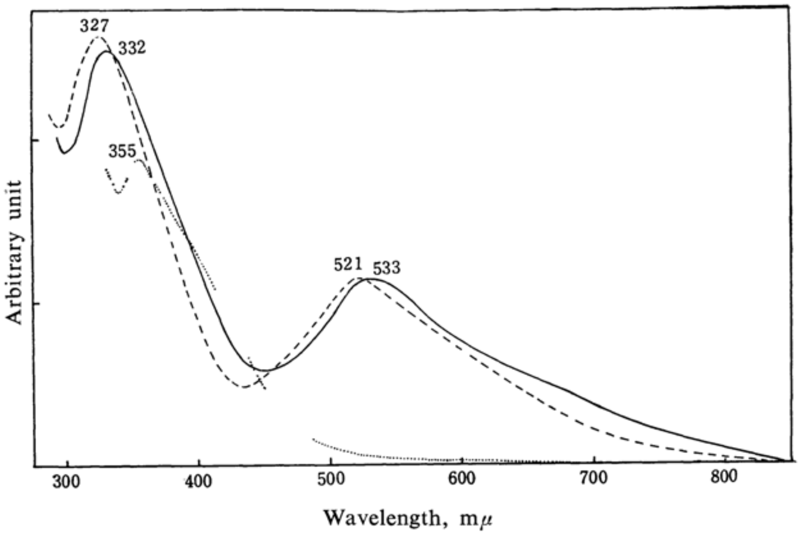

Fig. 2. The spectral responses of optical absorption and photoconduction for $\alpha,\alpha'$-diphenyl-$\beta$-picrylhydrazyl.
—— Absorption spectrum of solid (film)
---- Absorption spectrum of benzene solution
…… Photoconduction for sandwich-type cell

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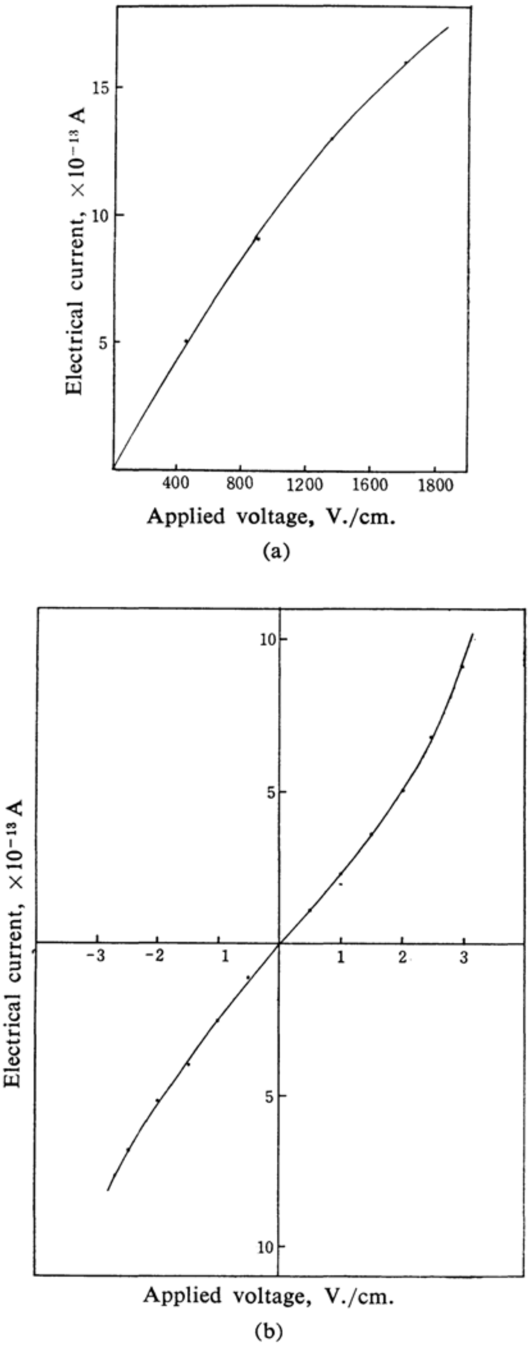
* The electrical resistivity, $\rho$, is expressed as $\rho=\rho_0 \exp(\Delta\varepsilon/2kT)$.

gap, $\Delta\varepsilon$. Hence, there should be a large difference in the mobility of charge carriers depending on the direction of the crystal.

Polycyclic aromatic molecules of thin film are in alignment with their ab plane with the film surface as reported in the previous paper[10]. The DPPH thin film is expected to be a similar behaviour. The anisotropic values of the resistivity of its two directions—the direction perpendicular to the film (sandwich-type cell) and that along to the surface (surface-type cell)—are also explained by the orientation of unpaired electron orbitals.



(a)

(b)

Fig. 3. The current-voltage relation of DPPH thin film cells.

(a) I-V curve of the surface type DPPH cell.

(b) I-V curve of the sandwich type DPPH cell.

A great difference was found on the characteristics of photoconduction and current-voltage relation in these two types of cells. The photoconduction for sandwich-type cell, Al||DPPH||Al[11], was found under an illumination of visible light but little for surface type one. The spectral response for photoconduction is illustrated in Fig. 2 as a dotted line.

In comparison with the absorption spectra of the DPPH crystal, which possess two absorption peaks, 332 and 533 m$\mu$, the spectral response for photoconduction is in a good agreement with that for optical absorption for the shorter wavelength peak of 332 m$\mu$, but not for the longer wavelength peak of 533 m$\mu$, which is completely missed in the response for photoconduction.

The variation of the current with the applied potential obeyed Ohm's law for the lower fields used. At the higher fields (over $10^3$ V./cm.), however, its voltage dependence was strongly curved for sandwich-type cell and became more linear for surface-type one as illustrated in Fig. 3.

## Summary

The electronic conductivity of two forms of $\alpha,\alpha'$-diphenyl-$\beta$-picrylhydrazyl, the single crystal and the thin film, was observed. The resistivity ($\rho_{15}$) at room temperature along c-axis ($1\times10^{10}\,\Omega$ cm.) is $10^5$ times lower than that perpendicular to the axis ($1\times10^{15}\,\Omega$ cm.), but its activation energy ($\Delta\varepsilon$) against temperature is in good agreement (1.5 and 1.6 eV.). These large anisotropy may be introduced from that of the arrangement of molecules in the crystal. In the case of thin film, the values of $\rho_{15}$ and of $\Delta\varepsilon$ are $\sim10^{10}\,\Omega$ cm., 1.7 eV. for surface type cell and $\sim10^{13}\,\Omega$ cm., 2.7 eV. for sandwich-type cell respectively. A great difference on the characteristics of photoconduction and on the current-voltage relation in these two types of cell was found.

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