# *The Spectral Dependence of the Photoconduction and the Mobility of the Charge Carrier in a Single Crystal of the Pyrene-Tetracyanoethylene Complex*

By Haruo KURODA, Keitaro YOSHIHARA and Hideo AKAMATU

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Photoconduction has been observed with solid molecular complexes involving polycyclic aromatic hydrocarbons as an electron donor and 1, 3, 5-trinitrobenzene (TNB), bromanil, or tetracyanoethylene (TCNE) as an electron acceptor.1) In the electronic spectra of these solid complexes, the absorption bands associated with the intermolecular charge-transfer excitation have been found in the visible region.2,3) We have shown in a previous paper1) that a weak photoconductive sensitivity in the wavelength region of the first charge-transfer band is appreciably dependent on the process of the crystal preparation, while the sensitivity in the shorter wavelength region is not. It seemed, therefore, that it would be interesting to examine the photoconduction with a well-grown single crystal of these complexes.

We obtained a single crystal of the pyrene-TCNE complex by slowly evaporating the solvent from a chloroform solution containing equivalent amounts of pyrene and TCNE. The crystal thus prepared showed a marked photoconductive sensitivity, a sensitivity much higher than that of various other charge-transfer complexes. We have examined the spectral dependence of photoconduction with a single crystal a few millimeters square and about one millimeter thick. The results obtained with a surface-type cell are shown in Fig. 1, together with the spectral dependence curve for a polycrystalline specimen which was grown from the melt of the complex. The spectral dependence curve of a single crystal rises steeply in the wave number region from 15000 to 20000 cm$^{-1}$. No photoconduction could be detected practically in the region corresponding to the first charge-transfer band, in contrast to the spectral dependence for a polycrystalline specimen. The threshold of photoconduction can be located at 13500 cm$^{-1}$ (1.67 eV.), a value which coincides with the energy gap, 1.5~1.6 eV., determined from the temperature dependence of the dark conductivity. It is evident, therefore, that the photoconduction observed in the lower wave number region with a polycrystalline specimen is not an intrinsic one.

The determination of the crystal structure of this complex is now in progress. The preliminary results show, that it is monoclinic, with the cell dimensions $a=14.58$ Å, $b=7.34$ Å $c=8.09$ Å and $\beta=92.4°$, and that it belongs to the $P2_1/a$ space group. Two molecules of pyrene and two molecules of TCNE are contained in a unit cell. The face of a plate-like single crystal is the bc plane, in which the transition moment of the charge-transfer excitation is nearly parallel to the c-axis. However no appreciable anisotropy was found in the dark conductivity or in the photoconductivity.

The drift mobility of the charge carriers in this complex was determined from the observation of the photocurrent pulse4) produced by an irradiation of a light pulse 1 $\mu$ sec. in duration from an air-gap spark. At room temperature, the drift mobility in the direction perpendicular to the bc plane was 0.15~0.2 cm$^2$/V. sec. for the electron and 0.05~0.08 cm$^2$/V. sec. for the positive hole. These values are smaller than the drift mobility of charge carriers in an anthracene crystal.4,5) We could

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1) H. Akamatu and H. Kuroda, *J. Chem. Phys.*, to be published.

2) H. Kuroda, M. Kobayashi, M. Kinoshita and S. Takemoto, ibid., **36**, 457 (1962).

3) H. Kuroda, K. Yoshihara and H. Akamatu, This Bulletin, **35**, 1604 (1962).

4) O. H. LeBlanc, Jr., *J. Chem. Phys.*, **33**, 626 (1960).

5) R. G. Kepler, *Phys. Rev.*, **119**, 1226 (1960).

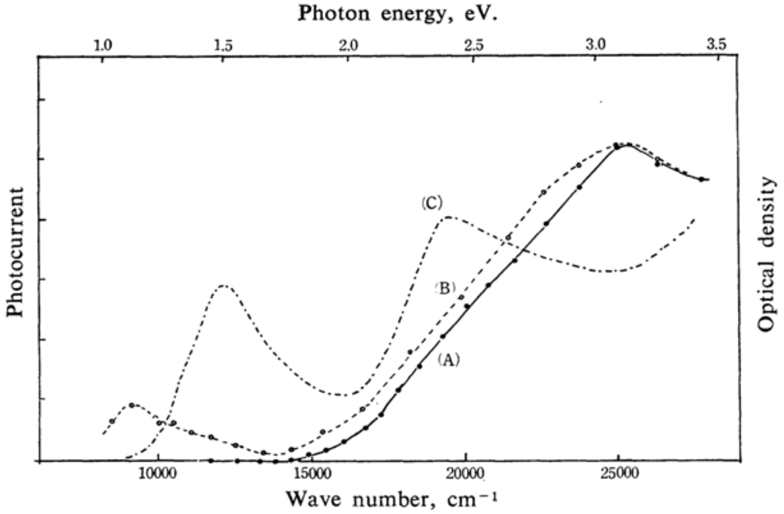

Fig. 1. Spectral dependence of photoconduction of pyrene-TCNE complexes. (A) Single crystal, (B) Polycrystalline specimen, (C) Absorption spectrum

not detect any appreciable change in the mobility from 5°C to 40°C. These results seem to indicate that the carriers in the pyrene-TCNE complex are of a more localized nature than those in anthracene or in other simple organic solids. This is quite reasonable if we suppose, as we have postulated in the previous papers,[2,3] that in the lowest conduction state of a solid molecular complex such as pyrene-TCNE, an conduction electron moves in the crystal lattice primarily by jumping from one acceptor molecule to another acceptor molecule, while a positive hole moves from one donor molecule to another donor molecule. The height of the photocurrent pulse was almost three times as much for the electron as for the positive hole. The stationary photocurrent was also higher when the light was irradiated through the negative electrode than in the reverse case. These results indicate that electrons make a larger contribution to the photoconduction than positive holes. This is probably the result of the difference in mobility.

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