Semiconductivity and Color of Pyranthrene

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The color of pyranthrene is a reddish brown. However, in the process of purification by a sublimation method, a yellow-colored pyranthrene is often obtained. When pyranthrene is sublimed slowly in the relatively high vacuum of 10^{-4} mmHg, a brown powder is obtained, whereas rapid sublimation in a low vacuum ($10^{-1}\sim10^{-2}$ mmHg) produces a soft yellow powder. The latter is also obtained when a molten sample is vaporized onto a cold glass plate. These two forms of pyranthrene with different colors can be changed to each other by the sublimation procedure; thus, we can obtain the yellow powder from the brown one, and vise versa.

The semiconductivities of these two forms of pyranthrene are of interest in relation to their crystal structures and absorption spectra; this paper will concern itself with these questions.

Pyranthrene was obtained from pyranthrone by zinc-dust fusion.[1] It was purified by a combination of repeated sublimations in vacuo and prolonged boiling in benzene. The two forms of powder were prepared by the procedure described above. A film specimen for each form was also made on a glass plate by a sublimation procedure in the way mentioned above. A single crystal, approximately $5\times0.1\times0.03$ mm^3, was grown in a sealed glass tube by a slow sublimation method. This crystal is brown in color.

The electrical resistivity (ρ) was measured by means of a dc method as a function of the temperature, which ranged from 40 to 200°C for the single crystal, both compressed powders (with the pressure of 116 kg./cm^2) and film specimens in vacuo. The results are summarized in Table I, where the ε-value, the energy gap or twice the activation energy for conduction, can be observed to be definitely lower for the yellow form than for the brown form.

TABLE I. SEMICONDUCTIVE DATA FOR PYRANTHRENE

		ε, eV.	$\rho_{15°}$, Ω·cm.
Single crystal		1.8	1.4×10^{15}
Powder	Brown	1.6	1.7×10^{16}
	Yellow	1.2	1.3×10^{14}
Film	Brown	1.7	7.3×10^{14}
	Yellow	1.1	3.0×10^{16}

The absorption spectra of pyranthrene in a solid state and in a solution are shown in Fig. 1. Both forms of pyranthrene gave the same absorption spectrum when they were dissolved in benzene. However, film specimens of two forms gave different spectral curves. The brown form exhibited its absorption maxima at 516, 468, 429 and 358 mμ, while the yellow form showed its maxima at 491, 417 and 358 mμ. The absorption at 358 mμ corresponds to the β-band of the molecular spectrum, while the others correspond to the para-band. However, when a KBr-disk technique was employed for the powder specimens, both forms gave the same spectral curve, with absorption maxima at 498, 449 and 425 mμ. Furthermore, both forms exhibited the same fluorescence spectrum.

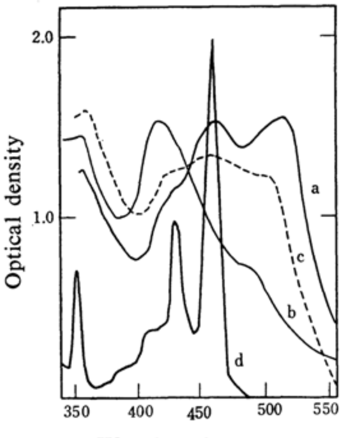

Fig. 1. Absorption spectra of pyranthrene.
(a) Brown film
(b) Yellow film
(c) KBr-disk of powder
(d) Solution in benzene

X-ray diffraction patterns for the powder specimens were obtained with the aid of a diffractometer. The patterns are shown in Fig. 2, which shows that the reflection peaks of the brown form are sharp and distinct, while those of the yellow form are very broad and diffuse. However, the crystal structure may be assumed to be the same for both forms.

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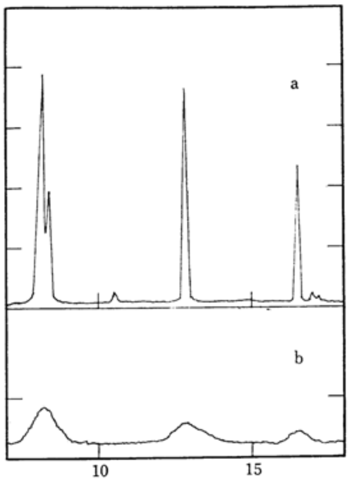

Fig. 2. X-ray diffraction patterns of (a) brown form and (b) yellow form (CuK_α).

An electron microscope revealed that both forms of powder and film specimens consist of flake-like minute crystals. The electron diffraction gave the same powder pattern for both forms of specimen; however, intensive spots could be observed in the reflection rings for the brown form but not for the yellow form.

All of these observations lead to the conclusion that the principal structure is the same for these two forms of pyranthrene, but that they result from different degrees of crystallinity. The yellow form consists of crystallites less perfect than those of the brown form.

The variation in apparent color may be explained mainly by the effect of the light scattering, which varies with the mode of aggregation of crystallites and hence depends on their crystallinity.

It is of interest to see that different semiconductive data were obtained for two forms of pyranthrene. If it can be assumed that the observed value of ε for the brown form corresponds to the intrinsic energy gap for pyranthrene, the lower value of activation energy observed for the yellow form can be related to an extrinsic conduction process which is associated with imperfections in the crystal.

Northrop and Simpson²⁾ and Parkyns and Ubbelohde³⁾ have observed the effect of impurities on the semiconductivity of organic crystals. Inokuchi and Ohki⁴⁾ have shown that the semiconductive data for pyrene varied according to the purification procedures. Eley and Parfitt⁵⁾ and Wihksne and Newkirk⁶⁾ have found that the semiconductivity of phthalocyanine changes with the transformation of the crystal structure. The present investigation has found an example of the semiconductivity of an organic crystal which is structure-sensitive and which varies with its crystallinity.

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