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Photoconductivity Of 1, 3, 5-Trithiane Single Crystals

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PHOTOCONDUCTIVITY OF 1,3,5-TRITHIANE SINGLE CRYSTALS.

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In continuation of the study of sulphur compounds^{1,2,3} we were led to examine the electrical behaviour of 1,3,5-trithiane. We think that the photoconductivity of single crystals of 1,3,5-trithiane is mainly extrinsic. The photocurrent action spectrum shows a maximum at 235 nm, the intensity of which varies appreciably with the presence of defects introduced onto the surface by means of thermal treatments or ageing. The dependence of the photocurrent on the incident light intensity is found to be sublinear.

EXPERIMENTAL

Commercial trithiane (Fluka purum) was purified by repeated crystallizations, continuous adsorption chromatography,⁴ and vacuum sublimation.

Trithiane crystals in the form of prisms were grown from benzene solution or by vacuum sublimation. Under the polarizing microscope only clear single crystals of good quality were selected, and from these a suitable portion was cut out

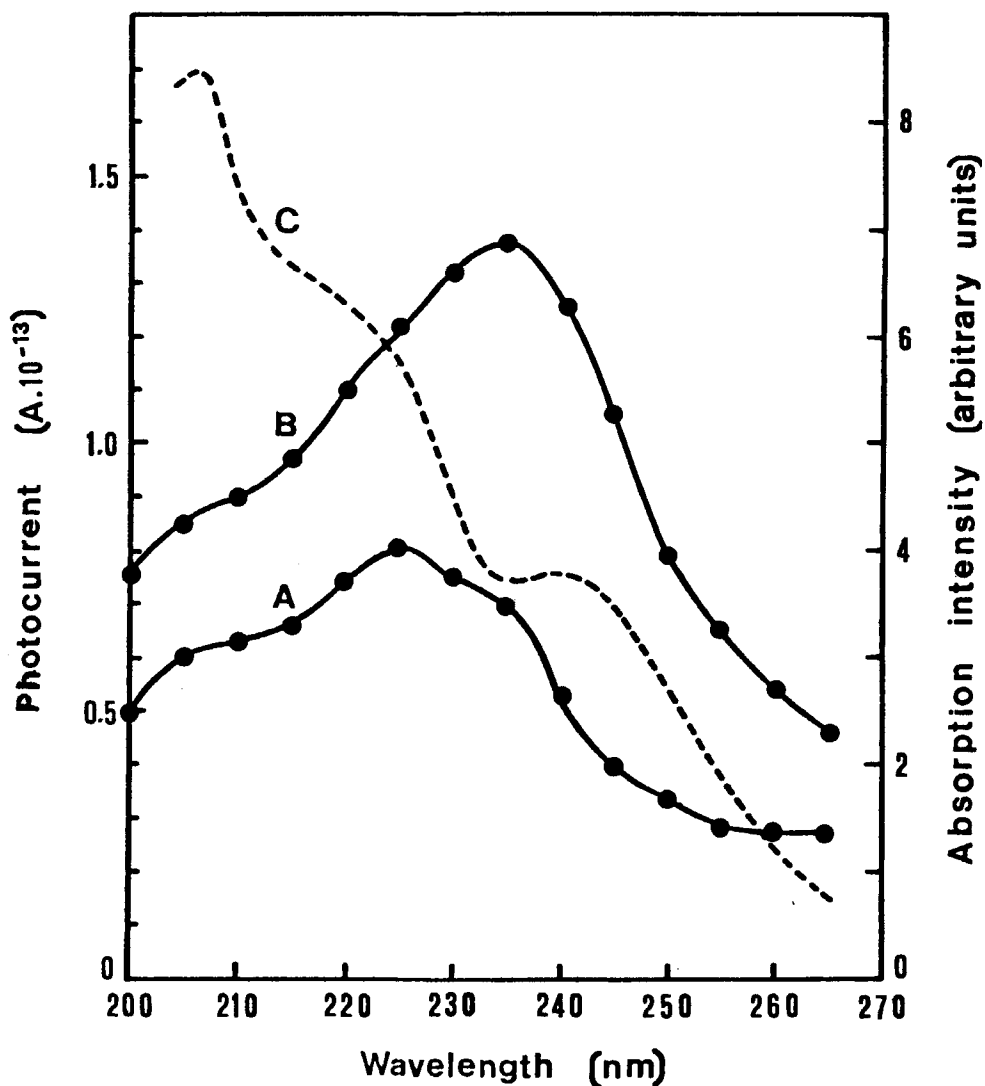


FIGURE 1 Spectral dependence of photocurrent: A = virgin crystal, B = thermally treated crystal, C = absorption spectrum (polycrystalline film).

(length about 2.5 mm and cross-section between 0.3 and 1 mm²). The crystals were kept in the dark and in an anhydrous atmosphere.

The d.c. steady-state measurements were carried out by a volt-amperometric method in an atmosphere of flowing nitrogen. The sample and the electrodes

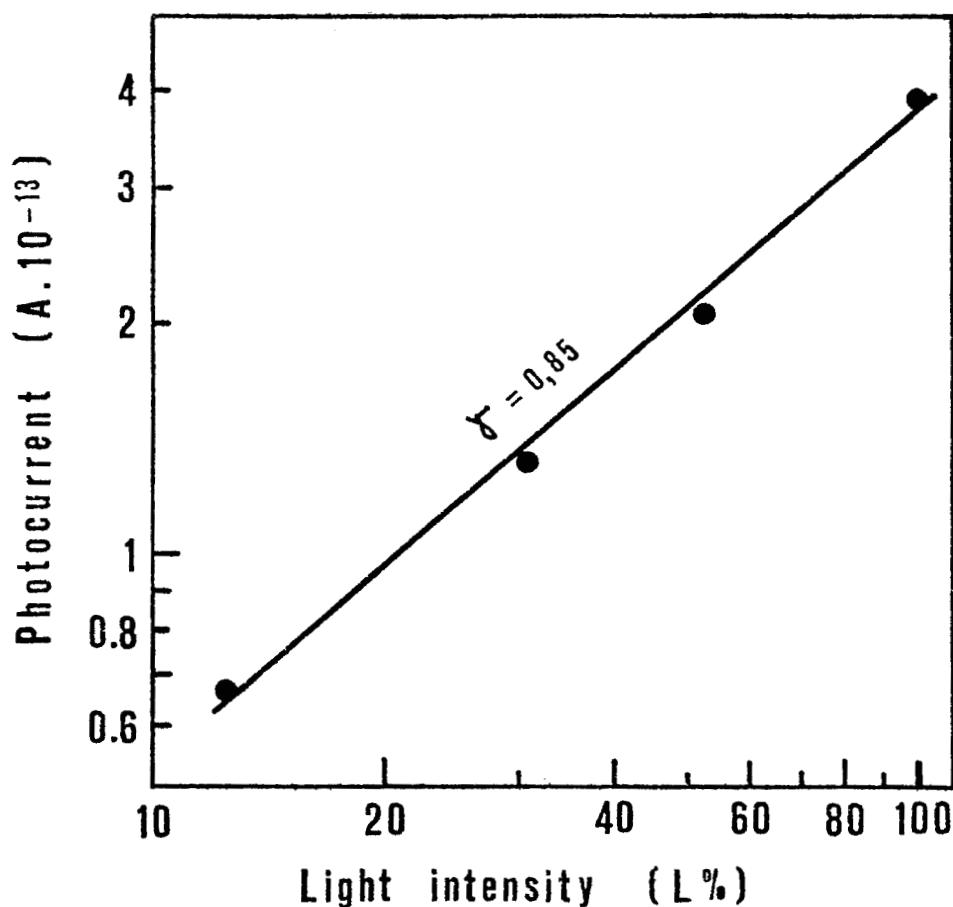


FIGURE 2 Dependence of photocurrent on light intensity. $L = 100\%$ corresponds to $24 \mu\text{W}/\text{cm}^2$.

(silver paint) were uniformly irradiated with monochromatized light.

RESULTS

The electrical resistivity of trithiane is of the order of 10^{15} ohm cm. We may observe that since what we measure is mainly a surface current, it is natural to expect that it mainly reflects the state of the surface.

The introduction of surface defects by means of

repeated thermal treatments up to 80°C in an atmosphere of nitrogen, by partial sublimation under reduced pressure, or by ageing leads to a change in the photocurrent action spectrum, as shown in Fig.1, which also gives the absorption spectrum in the solid. It is in fact observed that while in virgin crystals the photocurrent peak at 225 nm is prevalent, in crystals treated as described or aged there is an increase in the peak at 235 nm, which must therefore be attributed to the presence of surface defects.

At present it is not clear if the action spectrum of virgin crystals and the absorption spectrum must be considered similar or not.

The dependence of the photocurrent I_{ph} on the light intensity L , in the range of intensities from 3 to 24 $\mu W/cm^2$, which we examined with an applied field of 10,300 V/cm, is shown in Fig. 2 and is of the type:

$$I_{ph} \propto L^\gamma$$

with $\gamma = 0.85$, in agreement with that generally observed for organic photoconductors containing traps.

From the results obtained it is possible to say that the photoconductivity values of 1,3,5-trithiane must be attributed mainly to surface defects. We propose to demonstrate a possible intrinsic photoconductivity by observing whether in trithiane, as in many other compounds,⁵ the presence of sulphur is important for the purposes of electrical conductivity.

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