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A study of optical absorption in 9,10-anthraquinone crystals

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Single crystals of 9,10-anthraquinone having dimensions 5 mm × 5 mm × 1.5 mm were grown from the melt using the Bridgeman technique. The starting material was purified by sublimation and zone-refining techniques in specially designed crystal-growth tubes. The crystals were transparent and yellow in colour, and could be cleaved easily along *ab*-, *bc*-planes and poorly along the *ac*-planes of the crystal. Thin layer chromatography of the final crystals was performed, and no impurity was detected in these crystals by this technique. The cleaved crystals were found to have a surface photocurrent of $\sim 10^{-11}$ A, which increased non-linearly with the increasing voltage at room temperature. This is attributed to the formation of triplets in the bulk of the crystal which migrate and dissociate at the surface of the crystal. The optical absorption spectrum in benzene and ether solutions were found to exhibit similar behaviour in the visible range, i.e. 320–450 nm. From the optical absorbance data, the optical band gap was found to be ~ 3.4 eV.

1. Introduction

Single crystals of 9,10-anthraquinone can be grown from the vapour phase, from the melt, and from its saturated solutions. Selection of the suitable method depends upon the melting point, crystal structure, and chemical properties of the material, as well as on the required shape and size of the crystals [1]. It is known that 9,10-anthraquinone crystals grown from the solution and the vapour phase are needle-like [2]. It was observed by Bree and Lyons [3] that needle-like crystals of 9,10-anthraquinone do not provide a measurable photocurrent due to the small size of the crystals. This behaviour could be verified by using bulky single crystals.

In the present study, the final bulky crystals were examined by thin layer chromatography (TLC) for determining the purity of the crystals. The comparison of the optical absorption data of the "home-grown" crystals with other published work [4], and the voltage dependence of surface photocurrent is also presented. The present study was undertaken because there has been a marked increase in interest in the field of organic photoconductors [5], which are commonly used as dyes.

2. Experimental procedure

The bulky single crystals of 9,10-anthraquinone were grown using the Bridgeman crystal growth (BCG) technique. The material was purified by sublimation and zone-refining techniques. For the sublimation process, a Pyrex combination assembly tube type-A [6, 7] as shown in Fig. 1 was used and evacuated to a residual pressure of 10^{-3} torr (1 torr = 133.322 Pa) [8].

For zone refining, 15–17 zones were passed down through a 130 mm long column of the material. This took about 240 h. The temperature of the heater was adjusted to obtain the melting point of 9,10-anthraquinone which falls in the range 280–285 °C. The whole process of zone refining was repeated until no black impurities were detected. It was observed that during zone refining, 9,10-anthraquinone formed needle-like crystals.

The single crystals of 9,10-anthraquinone were grown using a resistance-heated furnace Type 365 (Cambridge Instruments Ltd, UK). The optimum condition found for anthraquinone growth in the preliminary trials was a steep temperature gradient with upper and lower ends of the furnace at 300 and 240 °C, respectively. The temperature was uniform over 20 mm length above and below the ends of the heating elements, as shown in Fig. 2. The rate of lowering the crystal growth tube was 1 mm h^{-1}. Continuous lowering through the temperature gradient resulted in crystal growth. When all the melt in the crystal growth tube had changed to a crystal, the lowering motor and the furnace were switched off to allow natural cooling of the crystal boule overnight.

A small quantity of 9,10-anthraquinone single crystal was dissolved in 30 ml benzene at about 80 °C. The absorption spectrum of this solution at room temperature was taken using a Spectronic 20, visible spectrophotometer (Bausch and Lamb, UK). The surface

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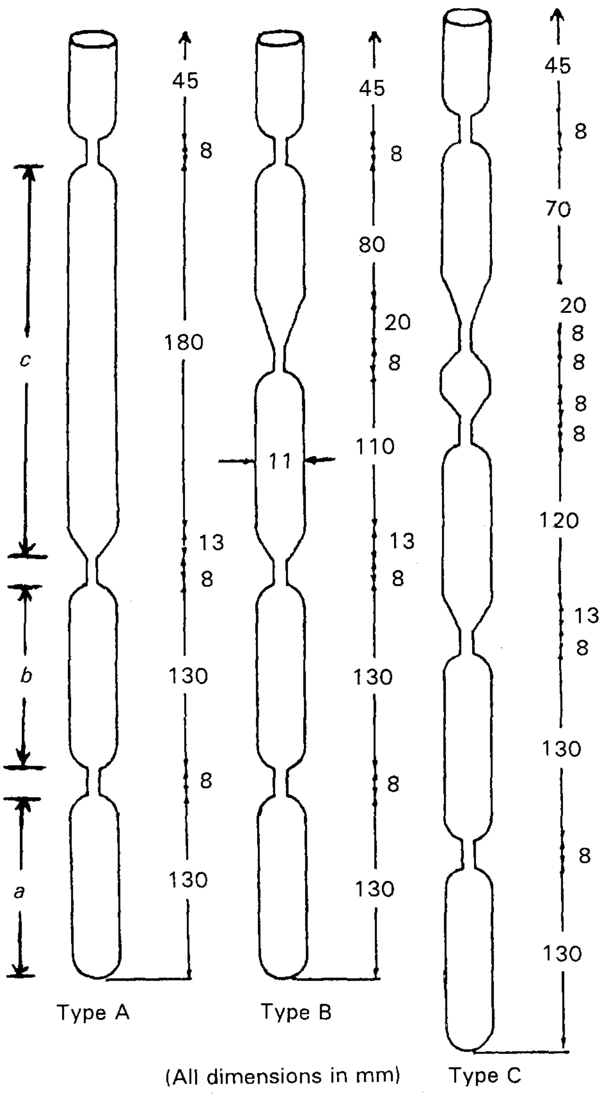

Figure 1 Combination tube assembly for the growth of 9,10-anthraquinone single crystals.

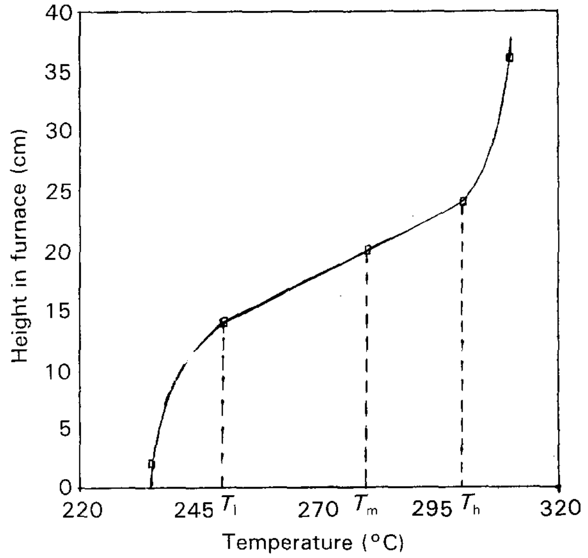

Figure 2 Temperature distribution in a Bridgeman crystal growth furnace type 365.

photocurrent of 9,10-anthraquinone single crystals having dimensions 5 mm × 5 mm × 1.5 mm was measured at a wavelength of 383 nm using a Keithley 610-C Electrometer, and an Ortec d.c-regulated power supply was used to apply voltage to the crystal specimen over a range of 300 V.

3. Results and discussion

A typical home-grown bulky single crystal of 9,10-anthraquinone (Fig. 3) was transparent and yellow in colour having its cleavage planes as shown in Fig. 4.

It was experimentally found that if the angle of the capillary to the vessel axis is less than 45°, the *ab*-cleavage plane will grow parallel to the vessel axis, but if this angle is greater than 45°, the *ab*-cleavage plane will grow perpendicular to the vessel axis. Other factors which affect the crystal orientation during crystal growth have been discussed in detail by Scott *et al.* [9].

It is well known that the rate of crystal growth sets an upper limit to the rate at which the crystal growth vessel can be lowered in the furnace. A rate of 1–2 mm h^{-1} as an upper limit for the growth of organic crystal is recommended in the literature [9]. In the present study, a speed of 1 mm h^{-1} (2.4 cm day^{-1}) was used to grow single crystals of 9,10-anthraquinone 35 mm long and 8 mm diameter. However, a rate greater than 1–2 mm h^{-1} resulted in the formation of polycrystals. Moreover, it was found that the type-B vessel was the most suitable for the growth of 9,10-anthraquinone single crystals. Furthermore, the wall of the growth vessel above the constriction should be sloped fairly gradually rather than abruptly outwards to the full diameter [8].

The crystal ingot, 35 mm long and 8 mm diameter, could be cleaved easily long *ab*-plane into platelets of 5 mm × 5 mm × 1.5 mm. Attempts to cleave crystal specimens less than 1.5 mm thick proved unsuccessful. These platelets were examined under the microscope for singularity and were found to be free from all striations and visible imperfections.

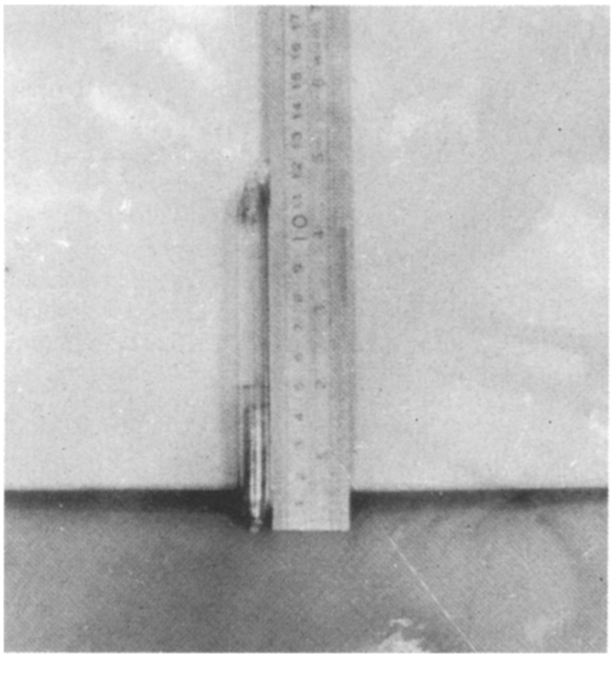

Figure 3 Home-grown bulky single crystal of 9,10-anthraquinone.

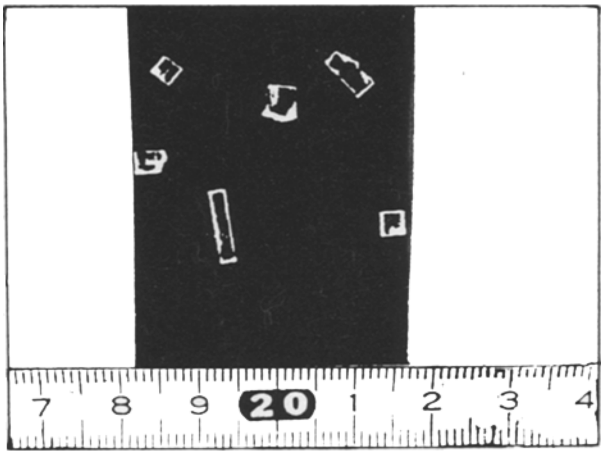

Figure 4 Anthraquinone single crystals showing cleavage planes.

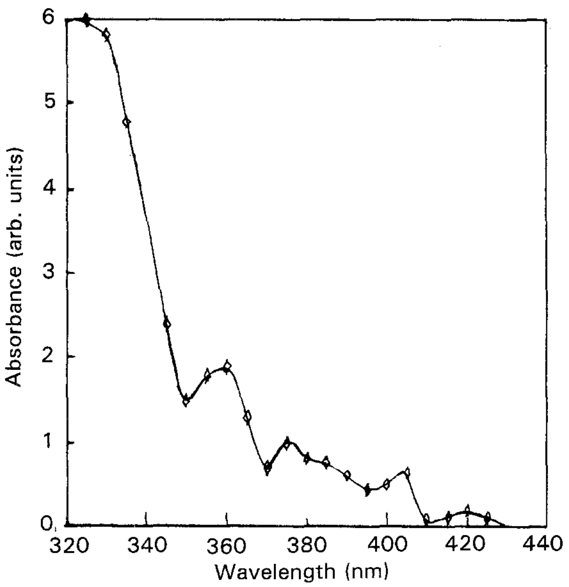

Figure 5 Optical absorption spectrum of 9,10-anthraquinone single crystal in benzene solution.

The purity of the crystals was checked by thin layer chromatography (TLC). For this purpose, a small piece of a "home-grown" single crystal of 9,10-anthraquinone and a small quantity of commercial grade pure 9,10-anthraquinone obtained from Kanto Chemical Co. Inc. Tokyo. Japan, were separately dissolved in hot dimethyl formamide (DMF) to form different solutions for micro-spotting. The rate of flow of the two materials (in the form of dry spots) was checked in different solvents; 100% MeOH, 99% MeOH + 1% $CHCl_3$ and 98% MeOH + 2% $CHCl_3$, respectively. Only a single spot and the same RF values for both the crystal specimen and for a small quantity of commercial grade pure 9,10-anthraquinone dissolved in the solvents mentioned above, were observed. It was found that the single crystal specimen grown using the BCG method has high purity.

The optical absorption spectrum of a "home-grown" 9,10-anthraquinone single crystal in benzene is shown in Fig. 5. The observed absorbance peaks for "home-grown" crystals in benzene and ether solutions [4] were found to be similar in the visible region (see Table I). Four absorption peaks corresponding to the n–π^* transition were observed in the wavelength region 377–420 nm in ether solution [10], whereas in the present study, four absorption peaks corresponding to the n–π^* transition were observed in the wavelength region 355–420 nm. Photo-carrier generation in single-crystal specimens of 9,10-anthraquinone illuminated by monochromic radiation takes place in the visible region in the wavelength range 380–410 nm. In this range, the photocurrent is correlated with the n–π^* transition of molecules due to weak optical absorption [10]. The optical band gap for 9,10-anthraquinone single crystal was also calculated from the extrapolation of the graph between photon energy ($\hbar\omega$) and $(\alpha\hbar\omega)^{1/2}$ as shown in Fig. 6. The band gap was found to be ~ 3.4 eV, and is in agreement with the other published data [11,12].

The plot of photocurrent versus applied voltage for a surface type cell is shown in Fig. 7. The photocurrent showed a non-ohmic voltage dependence and increased non-linearly with increasing voltage. No indication of the saturation of photocurrent with applied voltage was observed. Similarly, no indication of the dielectric breakdown was found up to the applied range of field strengths $\sim 2\,\mathrm{kV\,cm^{-1}}$. It was found that this behaviour of photocurrent was a function of the applied field only, and not of the distance between the surface contacts on the crystal. The departure from the ohmic behaviour could be due to the formation of

TABLE I

Absorbance peaks in ether [9] (nm)	Present study (benzene) (nm)
323.5	325
–	360
377	375
397	–
406	405
420	420

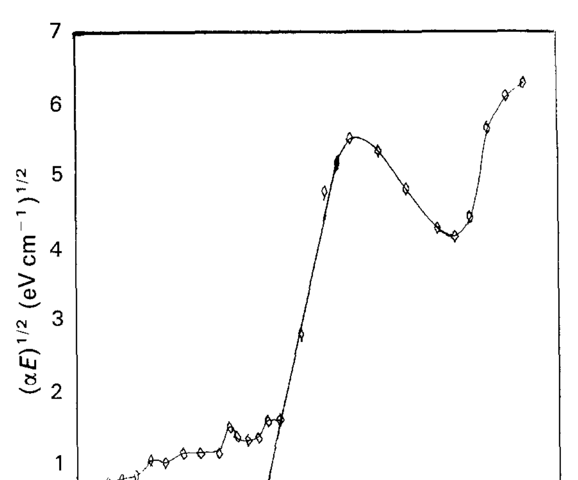

Figure 6 A plot of photon energy and $(\alpha\hbar\omega)^{1/2}$ for 9,10-anthraquinone single crystal at room temperature.

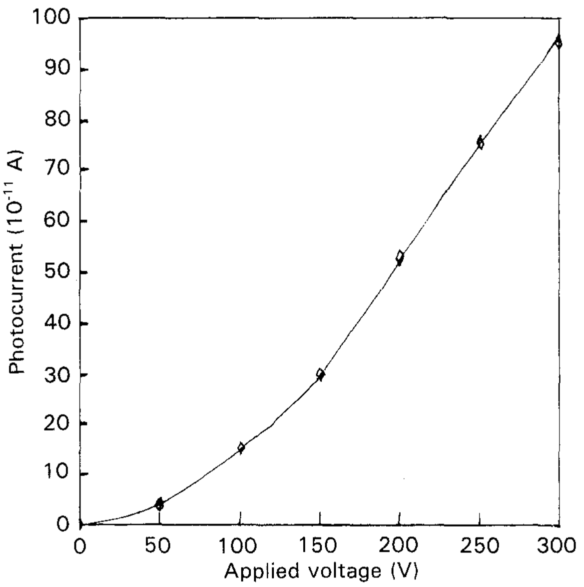

Figure 7 Voltage dependence of surface photocurrent for 9,10-anthraquinone single crystal at $\lambda = 383$ nm.

triplets at wavelength ~ 383 nm in the bulk of the crystal specimen which migrate to the surface and dissociate eventually [12]. It may be noted that at wavelength ~ 383 nm and above, the carrier generation in the bulk is not only due to the generation of triplets but also due to exciton–exciton collisions [13] and photoionization of excitons [14]. The optical absorption below the wavelength ~ 383 nm is very strong, and should yield a high number of carriers and hence a large photocurrent, but a few carriers are left in the bulk of the crystal because of the rapid recombination of carriers, thus producing a smaller photocurrent. Carriers formed at any depth in the crystal depending on the photon energy will move either into a region of higher recombination or a region of lower recombination on the application of the field to the crystal specimen. Higher recombination of carriers will yield a lower life time of the carriers and a smaller photocurrent [5].

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