Photo- and Semi-conductance of Organic Crystals. Part I. Photo-effects in Tetracene and Anthracene.

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Tetracene single crystals have been found to display a photoconductance effect in both the visible and the ultraviolet region. This effect, similar to that in anthracene, is promoted by the presence of air or oxygen, and removed by replacing the air with nitrogen. Thus it is concluded that the photoconductance is a surface phenomenon, in agreement with Lyons's theory to explain the spectral dependence. The photocurrent is in either crystal directly proportional to the applied field and also to the light intensity. Variations of current with time and with changed area of illumination are also reported. Naphthalene and phenanthrene gave no detectable currents under similar conditions to the others, and the theory is advanced that photoconductance varies with ease of aerial oxidation, increasing with ascent of the series naphthalene, anthracene, tetracene. Currents were found to be greater with tetracene than with anthracene.

Photoconductance in organic crystals is well known but no previous work has been performed on tetracene. Byk and Borck (*Ber. deut. phys. Ges.*, 1910, **8**, 621) and Volmer (*Ann. Physik*, 1913, **40**, 775) mention photoconductance in anthracene but the work in this period provided little knowledge of the actual processes involved. Since 1945 a number of workers have studied the photo- and semi-conductance of organic substances in the solid state, and in particular Szent-Györgyi (*Nature*, 1946, **157**, 857) has studied photocurrents in dyed proteins; Vartanyan (*J. Phys. Chem., U.S.S.R.*, 1946, **20**, 1065; *Acta Physicochim., U.R.S.S.*, 1947, **22**, 201; *Zhur. fiz. Khim.*, 1948, **22**, 770; 1950, **24**, 1361; 1953, **27**, 272; *Doklady Akad. Nauk S.S.S.R.*, 1950, **71**, 641) has examined semi- and photo-conductance in various dye molecules and mentions anthracene photoconductance, but we have found no detailed report of studies on anthracene. Nelson (*J. Chem. Phys.*, 1951, **19**, 798; 1952, **20**, 1327; 1954, **22**, 885) has confirmed and extended Vartanyan's work on dyes, and semiconductance in anthracene and certain other aromatic compounds has been observed by Eley (*Nature*, 1948, **162**, 819) and Eley, Parfitt, Perry, and Taysum (*Trans. Faraday Soc.*, 1953, **49**, 79) and by Mette and Pick (*Z. Physik*, 1953, **134**, 566) and Akamatu and Inokuchi (*J. Chem. Phys.*, 1950, **18**, 810). Preliminary reports of some of the work discussed in this series of papers have already appeared (Carswell, *J. Chem. Phys.*, 1953, **21**, 1890; Bree and Lyons, *ibid.*, 1954, **22**, 1630; Lyons, *ibid.*, in the press), and a suggestion that photo- and semi-conductance in anthracene-like crystals are closely related has been made by Carswell, Ferguson, and Lyons (*Nature*, 1954, **173**, 736). Since our first reports appeared the photoconductance of anthracene has been discussed by Chynoweth and Schneider and by Chynoweth (*J. Chem. Phys.*, 1954, **22**, 1021, 1029). However, the differences between their procedures and ours are considerable, and accordingly the results are to a large extent complementary. For example, we have worked with monochromatic light and studied the spectral distribution of the photoconductance: the Canadians have emphasised other features.

In the present experiments the crystals were prepared as thin sublimation flakes, and were mounted directly on to the electrodes and touched nothing else. The Canadians used much larger crystals, over 0·1″ thick, and mounted them in " sandwich " and other cells with a supporting base for the crystal. Since the phenomenon is now known to involve surface effects, we feel it is valuable to have results from a variety of experimental procedures. A further difference between the Canadian work and ours is that we have examined the currents obtained at rather lower values of the electrical field applied across the crystal.

When this work was begun in 1950, existing results had all been obtained with polycrystalline materials, and mostly on substances for which neither phenomenon of light absorption nor the crystalline structure was well understood. This we judged to be a handicap in understanding photoconductance. Although even now the spectrum of anthracene crystals has not been interpreted completely, yet a good deal is known about it (see Craig, *Rev. Pure Appl. Chem.*, 1953, **3**, 207); since, in addition, the crystal structure of anthracene has been determined in detail (Robertson, " Organic Crystals and Molecules," Ithaca, New York, 1953), and also as anthracene has a considerable number of mobile electrons, it was chosen for the initial work. However, it will be shown that the phenomena observed and the techniques used are not confined to anthracene (*e.g.*, tetracene behaves very similarly) and the conclusions emerging from the work should often be transferable also to the dyes field.

The work has taken on a number of different aspects but, as the basic experimental methods were often constant, they are described for the most part in this first paper.

EXPERIMENTAL

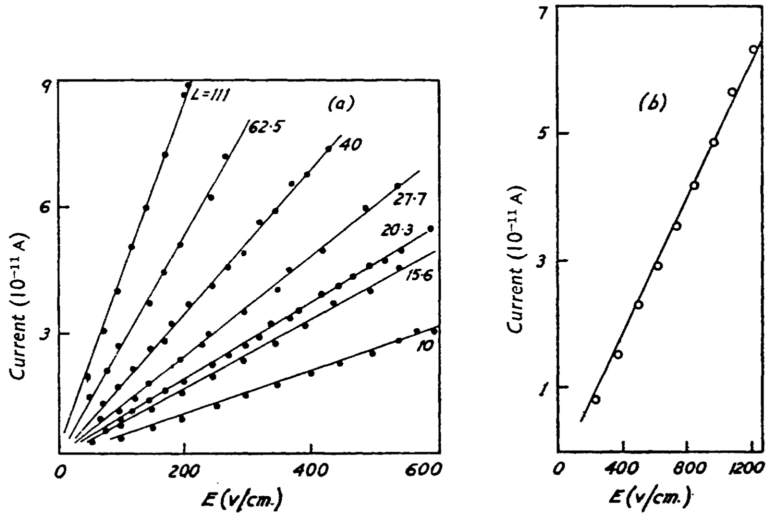
The anthracene was first thoroughly purified by azeotropic distillation of 50 g. with 750 c.c. of ethylene glycol which had itself been purified previously. From the fraction of b. p. 197·5° anthracene was recovered by the addition of water. The process was repeated twice, and the final sample recrystallised from alcohol (m. p. 216°). Finally, to obtain the flakes used, sublimation was carried out from a well-lagged lipless 50-c.c. beaker covered with a perforated filter-paper and a crucible lid. Solid carbon dioxide was placed in the beaker some time before heating was commenced, in order to give a non-oxidising atmosphere. Fluorescence spectra, kindly taken by Mr. J. Ferguson, showed no trace of tetracene or other impurity. Certainly the purity was higher than that of a sample intended for use in a scintillation counter which was obtained and which had a yellow colour in a 1-cm. layer although fluorescing blue. The flakes obtained were frequently single crystals many of which showed interference colours. Any one crystal showed but a single colour which varied with the crystal thickness. The tetracene was obtained from a commercial sample, resublimed under nitrogen and spectroscopically free from other absorbing substances such as anthracene. Sublimed flakes were single crystals. Two methods of mounting were used: (*a*) The crystal was laid flat upon a silica disc with contacts made through " Aquadag " on the top surface; (*b*) the crystal was mounted between two platinum wire electrodes, spaced about 2 mm. apart. In both cases the electrode leads were held on a framework of stout copper wire mounted in a large rubber stopper which served as an insulating base. The whole of this electrode assembly was about 3″ high and was portable. In (*b*) the crystal was attached to the platinum by means of a solution of " Aquadag," a suspension of carbon in water. The " Aquadag " as bought was diluted by about 1 : 1 and painted on the electrodes, after which the crystal was laid across the wires, and the whole allowed to dry. The crystal was now firmly attached to the wires, and the electrode assembly moved into position in a metal box where connections to the amplifier were made. This method of mounting, with the crystal surfaces not touching any supporting surface, except at the edges where the electrodes made contact, was chosen to avoid any possible electrical leak along the supporting surface and to ensure that any current that did not flow through the surrounding gas certainly did pass through the crystal itself. The light was incident on that side of the crystal to which the electrodes were connected.

The metal box with two compartments was made to be screwed to the monochromator of a Beckman Spectrophotometer (Model DU). One compartment was so placed that the light beam entered it through a centrally positioned fused silica window; and in this compartment were placed the electrode assembly and a phosphoric oxide desiccant. Invariably before any measurements were taken both compartments were dried. The final adjustment of the crystal into the light beam was done visually after removal of the back of the compartment.

In the second compartment was the amplifier, so arranged that in the top of the box both current and voltage meters were visible. The amplifier used a single-stage triode electrometer valve, ME1401, with a 10^{9}, 10^{10}, 10^{11}, or 10^{12} ohm grid resistor. Full-scale deflection on the 50 μA meter was obtained with a current in the grid (10^{12} ohm) circuit of *ca.* 7×10^{-13}A. The sensitivity was linear. The amplifier had a time constant of about 20 sec. with the 10^{12} ohm but very much less with the 10^{10} ohm resistor. The dark current was *ca.* 10^{-14}A, or about one-tenth of a typical photocurrent. Before any reading, a zero adjustment was made by compensation of the dark current.

The atmosphere surrounding the crystal was air dried with phosphoricoxide. The lamps used were the usual tungsten and hydrogen (300 mA) types supplied for the Beckman Spectrophotometer. These were used either in conjunction with the monochromator or with accompanying filters. The range of usefulness of the hydrogen lamp was confined to wavelengths above 2250 Å; at lower values the glass envelope did not transmit sufficiently to give appreciable currents. Above 3700 Å also the hydrogen-lamp emission curve showed maxima at 3790, 3875, and 4065 Å, minima at 3760, 3820, and 3915 Å (for a slit of 0·26 mm.). These intensity fluctuations were of the order of 5—10% of the average intensity over that wavelength range. Such considerations were important, since the first anthracene band system falls in the same range. Consequently, it was impossible to obtain a precise spectral dependence curve of the photoconductance without using two separate light sources. In taking an ordinary absorption spectrum the difficulty is not so important since it is then the ratio of incident to transmitted intensities which is of interest. With the photoconductance, however, one quantity of interest was the absolute value of the incident intensity; consequently, the best procedure is to determine the absolute output from each lamp at all wavelengths. The difficulties involved have so far prevented us doing this. But we have determined the relative intensities of light emitted at different wavelengths and this has enabled the recording of the results shown in Part II (following paper).

FIG. 1. *Photo-current, I, plotted against electric field, E.*



(*a*) *Tetracene suspended between electrodes; tungsten lamp.* (*b*) *Anthracene on silica; hydrogen lamp.*

Flaws in the Crystal.—In some crystals flaws were clearly visible. Very often these had the effect of destroying all photoconductance phenomena, and so only crystals which appeared perfect were used.

Current–Applied Potential Relation.—As reported earlier for anthracene (Vartanyan; Carswell; Chynoweth and Schneider, *locc. cit.*) the current varies directly with the applied potential in the range studied. Results for anthracene, exemplified by Fig. 1, show that such a linearity holds from 0 to 1200 v/cm. for the particular light intensity used. The field strengths shown in this paper are calculated simply by dividing the applied voltage by the distance between the electrodes, the assumption being made that the drop in potential from one electrode to the other is steady and that there is no sudden change near either of the electrode surfaces which invalidates such a calculation. At one time (Carswell, *loc. cit.*) it was thought that there were signs of a plateau in the current–voltage curve before the current rose steadily again, but further work has shown that the curve is linear in the manner shown. The results of the various workers are accordingly in agreement. The values shown here are often accurate only to within about 15% because of the difficulties of measuring the separation of the " Aquadag " contacts.

Tetracene was investigated in some detail and the results are shown in Fig. 1*a*. Once again a rigorous linearity is obtained for constant light intensity. The various curves of the figure demonstrate that simple proportionality holds for a wide variation in the incident intensity. The most obvious difference from the anthracene results is that the tetracene needs much lower voltages than anthracene to produce a given photocurrent. Alternatively the light intensity may be lower. This difference between the two compounds must be of importance in the final elucidation of the detailed mechanism and will be discussed later. The current–potential relation was of the same form with polychromatic light as with monochromatic.

The *current–light intensity relation* was studied in three different ways, depending on the method used to vary the light intensity. The results are shown in Fig. 2, *a* and *b*, for tetracene and anthracene, and it is seen that there is in all cases a simple proportionality between the current, *I*, and the light intensity, *L*. The three methods used to vary the light intensity were (*a*) moving the lamp from the crystal in measured steps; (*b*) inserting aluminised or silvered silica filters of known optical density; and (*c*) varying the slit on the Beckman spectrophotometer. In Fig. 2*a* a tungsten lamp of small filament size mounted behind an adjustable diaphragm was used, and the current with the lamp at the point of closest approach to the crystal is indicated by the encircled point at $L = 10$. The other circles indicate the currents when the lamp was moved away from the crystal by a known amount. An inverse-square law was used to calculate the relative light intensity : thus with the lamp at $\sqrt{2}$ times its original distance $L = 5$. The linear relation so obtained was checked by a combination of methods (*a*) and (*b*), and the results are shown on the same graph by enclosing the points in squares. Method (*c*) allowed measurements to be made with monochromatic light. The slit of the Beckman spectrophotometer controls both entrance and exit beams and so, for a sufficiently wide and uniform beam, doubling the slit width gives a fourfold increase in the emergent light. This, in turn, if completely incident on the crystal, would give a fourfold increase in photocurrent. Experiments were conducted on both anthracene and tetracene in which the light did fall completely on the crystal even with the slit most widely open. In every instance the linear relation between *L* and *I* was confirmed, *e.g.*, see Fig. 2*b*.

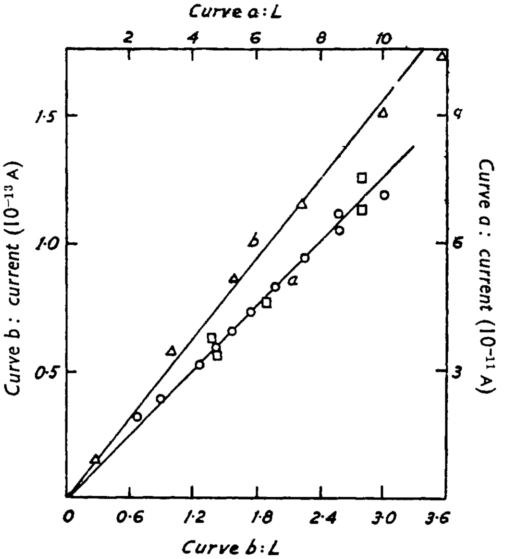


FIG. 2. *Photo-current, I, plotted against relative light intensity, L.*

○ *Intensity varied by moving lamp.*
□ *Intensity varied by inserting a silvered glass filter transmitting* 55%.
△ *Intensity varied by alteration of slit width and then moving lamp.*
(*a*) *Tetracene on silica, tungsten lamp,* (i) $E = 22$ v/cm.; (ii) $E = 60$ v/cm.
(*b*) *Anthracene suspended between electrodes,* $\lambda = 3900$ Å (*N.B. : change of L units*).

The *current–time relation* for anthracene reported by Vartanyan (*loc. cit.*) was not accompanied by sufficient experimental detail to judge whether it is an effect due to the apparatus or to the crystal. The current build-up after turning on the light was reported to be about 30 sec. This result is in apparent disagreement with that of Chynoweth and Schneider (*loc. cit.*), where the build-up was apparently nearly instantaneous, being less than the constant of the input circuit of the amplifier used (10^{-1} sec.). However, these workers, on increasing the light intensity, suddenly observed a build-up of current over a period which seems to be of the order of a minute (no quantitative results are given in their Fig. 6). Such a result is obviously not attributable to the amplifier, but the complete explanation is not clear.

Superimposed upon these short-term variations the Canadians observed a relatively slow build-up over periods of up to 30 min. Also, with anthracene, Carswell (*loc. cit.*) reported a slow build-up, but this was due largely to the circuit elements including the 10^{12} ohm grid resistor which was necessary to detect the feeble currents obtained with monochromatic light. This constant, defined as the time in which the current increased to 1/e of its maximum value, definitely depended on the circuit, being 20 sec. with the 10^{12} ohm resistor, 3 sec. with 10^{10} ohm, 1 sec. with 10^{9} ohm. The actual value depended, especially with the high resistances, upon the thoroughness with which the crystal had been dried. No sign of a decay from a quickly reached maximum was found except with one crystal, and this result could not be reproduced with other crystals. The particular mounting of the crystal and its previous history seem to make the results vary. With tetracene on a silica disc and with use of a 10^{10} ohm resistor the current meter came immediately to a steady value on every occasion. However, when current readings were recorded over several hours a very slow build-up of photocurrent was observed. At any point during this build-up, switching off the light caused the meter to read zero; re-illumination after a few seconds gave the same current as that measured before switching off. Thus the build-up was not due to some zero fluctuation but appeared to depend on a variation in the crystal condition which remained constant while the light was off for a few seconds.

Tetracene, when mounted directly across platinum electrodes with " Aquadag," and with a 10^{10} ohm resistor in the circuit, showed a slow build-up over 150 min., and typical curves are shown in Fig. 3 for a field of 500 v/cm.

FIG. 3. *Current build up in tetracene after switching on of light : two runs.*

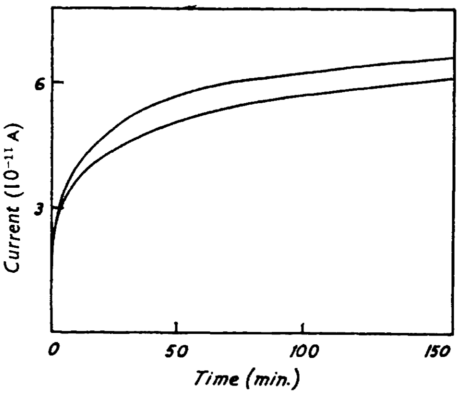
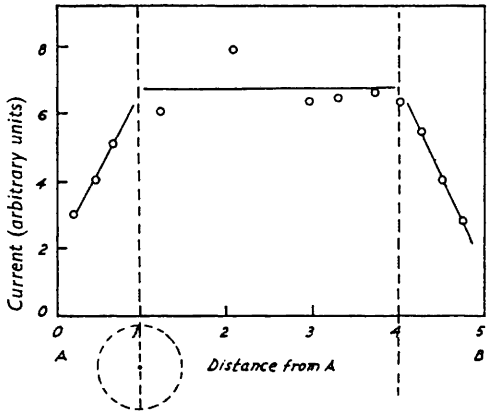


FIG. 4. *Effect of moving the light spot across the crystal from electrode A to electrode B.*



The broken lines mark the extremities beyond which only a portion of the light fell upon the crystal surface.
The circle indicates the size of the light spot.

The *effect of oxygen* on photoconductance of anthracene was discovered by Vartanyan (*loc. cit.*) and has been investigated by Chynoweth (*loc. cit.*). We have found that oxygen promotes photoconductance in tetracene, and have also obtained results in agreement with the other work on anthracene. Our early results on anthracene led us to test other substances including naphthalene and phenanthrene. Since there is a very close structural and spectroscopic similarity between these substances and anthracene it was thought that they too might show photoconducting properties. However, no current could be detected with either substance. Chemically, anthracene differs from the other two compounds in its much greater readiness to form a quinone upon oxidation. Sublimation of anthracene must be carried out in a non-oxidising atmosphere to prevent aerial oxidation (in this work, carbon dioxide was used), whereas the others may safely be sublimed in air. Consequently, it was thought that photoconductance and ease of oxidation might be linked. In order to test this hypothesis tetracene was examined, since its ease of oxidation is known to be greater than that of anthracene. As pointed out above, the photoconductance of tetracene is greater than that of anthracene at similar values of field and light intensity. It was accordingly stated by Bree and Lyons (*loc. cit.*) that photoconductance increases as the series naphthalene, anthracene, tetracene is ascended. This lays a basis for future work on the higher members of the series. It now seems that photoconductance in organic crystals is to be expected when there is the possibility of a combination with oxygen.

Such a combination need not be the complete formation of a quinone but could be some intermediate such as is formed by an association of the triplet oxygen molecule with the hydrocarbon molecular centre, itself possibly in a triplet state such as has been thought to occur in semiconduction (Part II, *loc. cit.*; cf. Bowen, *Discuss. Faraday Soc.*, **1953**, 14, 143; Carswell, Ph.D. Thesis, Sydney, 1954). Some such intermediate from anthracene has been postulated independently by Chynoweth (*loc. cit.*). Our results showed that on replacement of the oxygen atmosphere by an inert gas such as nitrogen or by a vacuum the photocurrent decreased, and *vice versa,* the process being reversible. It follows that the intermediate was not the quinone itself, which would be stable in air.

The effect of changing the area of illumination was studied by moving a small light spot across the crystal from one electrode, *A*, to another, *B*. The results are shown in Fig. 4. Where the light fell partly on to the " Aquadag " contact the current was reduced, but where the whole light fell upon the anthracene crystal it is seen that the current was independent of the position of the beam between the electrodes.

Irradiation in the infrared after switching off the ultraviolet source gave no measurable current increase, emphasising a difference in mechanism from certain inorganic photo-conductors. One crystal, exceptionally sensitive to the ultraviolet, was found which gave currents when irradiated with infrared of wavelength about 3 μ, but this result could not be repeated on other crystals.

DISCUSSION

Possibly the most important conclusion is that the photoconductance is a surface phenomenon, as Chynoweth has also concluded, although he found also a residual photoconductance *in vacuo.* Lyons (*loc. cit.*) found that the spectral dependence of the photoconductance can be explained if the phenomenon is a surface effect. This theory assumes that energy as an " exciton " must be transferred to the surface from the site where it is absorbed and becomes effective in producing a current only upon reaching the surface, since it is the surface layer which contains an anthracene–oxygen compound. Alternatively, the oxygen compound could be thought to increase the mean free path of the electrons and so increase the photocurrent, as Chynoweth suggests. To prepare and examine anthracene in a completely oxygen-free atmosphere would give interesting results, for if the carriers originate in the oxygen compound then such anthracene should give no current at all, and not merely a greatly decreased current as has been reported. However, if the carriers do not need an oxygen compound for their formation, some perturbation of the crystal field in the surface layer must be responsible for ionisation, since the spectral properties of anthracene do not indicate that internal ionisation takes place in the crystal. In a molecular crystal such as anthracene the intermolecular forces are small (Davydov, *Izvest. Akad. Nauk, S.S.S.R.*, 1950, **14**, 502), and so there should be no large change in the properties of molecules on the surface compared with those in the bulk. Accordingly, ionisation should not be expected in the surface if it does not take place in the bulk. Hence we conclude tentatively that the current carriers are formed by the transfer of energy to the anthracene–oxygen compound [unless some effect at the electrode boundary is the cause of ionisation, but there is no evidence at all for this: indeed, the constancy of the photocurrent with varying position of illumination shown in Fig. 4 is evidence of an opposed kind (cf. Chynoweth, *loc. cit.*)].

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