

**722.** *Photo- and Semi-conductance in Organic Crystals. Part III.*<sup>1,2</sup>  
*Photoeffects in Dry Air with Eleven Organic Compounds.*

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Photocurrents between  $10^{-10}$  and  $10^{-16}$  A in dry air were detected in single crystals of several aromatic organic substances which have a very high dark resistivity. Surface and bulk currents,  $I_S$  and  $I_B$ , were distinguished in anthracene which was considered typical. The dependence of  $I_S$  and  $I_B$  upon voltage, wavelength, time, light intensity, and area of illumination is reported. Space charges were found both at electrodes and over the area of a light beam shining between the electrodes. The quantum efficiency both of carrier liberation inside the crystal and of electron production in the outer circuit, the surface and bulk mobilities, and the mean free path are estimated. The mechanism of carrier liberation and the influence of surface double layers are discussed. It is suggested that both electrons and positive holes are trapped. A theory is advanced to explain the spectral dependence of  $I_B$ . The magnitude of the photocurrents is correlated with a number of other properties of the substances.

REFERENCES to earlier work on photo- and semi-conduction in organic crystals were given in Parts I and II.<sup>1,2</sup> Since then much further work has appeared on photoeffects<sup>3-9</sup> and on semiconduction<sup>5, 10-13</sup> in hydrocarbon crystals as well as much work on dye crystals.<sup>14-16</sup> Most of the hydrocarbon work has been done on anthracene, but the semiconduction of some solid solutions has been studied<sup>10</sup> and a brief mention has been made of a photoeffect in chrysene.<sup>8</sup>

This paper is concerned with the photoeffects in a range of hydrocarbon and related molecules, few of which have been reported previously as photoconductors, except in our preliminary publication.<sup>9</sup> Anthracene has also been studied further. The spectral dependence of the photocurrent is mentioned here only for anthracene: other substances

<sup>1</sup> Part I, Bree, Carswell, and Lyons, *J.*, 1955, 1728.

<sup>2</sup> Part II, Carswell and Lyons, *J.*, 1955, 1734.

<sup>3</sup> Zinszer, *Z. Naturforsch.*, 1956, **11a**, 306.

<sup>4</sup> Goldsmith, Ph.D. Thesis, Purdue, 1955.

<sup>5</sup> Inokuchi, *Bull. Chem. Soc. Japan*, 1956, **29**, 13.

<sup>6</sup> Schneider and Waddington, *J. Chem. Phys.*, 1956, **25**, 358.

<sup>7</sup> Bree and Lyons, *ibid.*, 1956, **25**, 384, 1284.

<sup>8</sup> Northrop and Simpson, *Proc. Phys. Soc.*, 1955, **68**, 974.

<sup>9</sup> Lyons and Morris, *ibid.*, 1956, **69**, 1162.

<sup>10</sup> Northrop and Simpson, *Proc. Roy. Soc.*, 1956, **234**, A, 124, 136.

<sup>11</sup> Many, Harnik, and Gerlich, *J. Chem. Phys.*, 1955, **23**, 1733.

<sup>12</sup> Pick and Wissman, *Z. Physik*, 1954, **138**, 436.

<sup>13</sup> Eley and Parfitt, *Trans. Faraday Soc.*, 1955, **51**, 1529.

<sup>14</sup> Vartanyan, *Doklady Akad. Nauk S.S.S.R.*, 1954, **94**, 829; *Zhur. fiz. Khim.*, 1953, **27**, 272; 1954, **8**, 856.

<sup>15</sup> Weigl, *J. Chem. Phys.*, 1956, **24**, 364, 577, 883.

<sup>16</sup> Nelson, *ibid.*, 1955, **23**, 1550; *J. Opt. Soc. Amer.*, 1956, **46**, 10.

will be discussed in a later paper. All behaved in general similarly to anthracene. We now report the dependence of the D.C. photocurrent on applied voltage, light intensity, electrode contacts, and area and time of illumination for single crystals in dry air. Both surface and bulk photocurrents were obtained. Anthracene, naphthalene, phenanthrene, chrysene, 1:2-benzanthracene, 1:2:5:6-dibenzanthracene, diphenyl, *p*-terphenyl, dibenzothiophen, and acridine all gave photocurrents. No current was obtained with hexamethylbenzene or 1:2:3:4:5:6:7:12:13:16-decahydropyrene.

#### EXPERIMENTAL

The D.C. amplifier<sup>17</sup> built around a Mullard ME1402 electrometer valve could detect less than  $10^{-16}$  A. Current gain was  $10^8$ , hysteresis effects were absent, and the time constant was 2 sec. (for a  $10^{11}$  ohm resistor) corresponding to the galvanometer period. The amplifier was calibrated for a grid voltage change of  $\pm 1.5$  v, being over the range  $\pm 0.25$  v. Random noise fluctuations corresponded to changes in grid bias of 100  $\mu$ v. The field applied to the crystal could be reversed. For the surface currents the "Alkadag" electrodes were connected to platinum wires mounted on a polystyrene support. Often the crystal was held only by the electrode leads but sometimes a silica disc was used as a support. Phosphoric oxide was used as desiccant since water vapour decreased the photocurrent. For currents through the bulk crystal a semitransparent aluminium surface provided one electrode. Light from a tungsten, mercury, or hydrogen lamp was polarized by a Wollaston prism after passing through the monochromator of a Beckman spectrophotometer; the electric vector of the light was made to lie along a crystal optical direction. The mercury lamp was calibrated by a Schwarz linear thermopile, and the other lamps were compared with the mercury lamp by means of an IP28 photomultiplier.

Anthracene, chrysene, diphenyl, *p*-terphenyl, acridine, and dibenzothiophen were purified by chromatography on aluminium oxide with light petroleum in a darkened room; for pyrene, see ref. 18. Naphthalene, purified with the aid of a Raney nickel catalyst, was kindly supplied by Mr. R. Redies. Phenanthrene was purified as described previously,<sup>19</sup> and the benzanthracenes by sublimation. Fluorescence measurements above 4000 Å on all substances except naphthalene recorded no peaks other than those reported in the literature.<sup>20</sup> Single crystals of the hydrocarbons were obtained by sublimation in an inert atmosphere, and those showing a twinning plane, obtained frequently with pyrene and phenanthrene, were discarded. The (001) face was that commonly developed but with 1:2:5:6-dibenzanthracene the (010) face appeared. Relatively large crystals (1 cm.  $\times$  1 cm.  $\times$  10  $\mu$ ) were obtained with diphenyl and naphthalene, but most of the crystals were about 3 mm  $\times$  3 mm  $\times$  5  $\mu$ . As the heterocyclic substances gave needles on sublimation, a mass of similarly oriented single crystals was used. All crystals were examined under a polarizing microscope for the identification of the optical directions, and those with visible flaws were rejected. Thicknesses were measured with an Ehringhaus compensator. Results with sandwich cells were confined to anthracene, which was the only substance available in a suitable form.

#### RESULTS

*Current-Time Relation.*—When other factors (*e.g.*, field, light intensity) are held constant the *I-t* (current-time) relation may be studied during the first fraction of a second, during the first minute, or during an hour or longer. Our equipment allowed us to study the last two cases, but a study during the first fraction of a second has recently been reported by Goldsmith<sup>4</sup> who found a build-up time for anthracene of about  $10^{-5}$  sec.

With the surface cell the rise of  $I_s$  (surface current) to a maximum,  $I_p$ , in *ca.* 2 sec., followed by a fall to an approximately constant value,  $I_c$ , was obtained either with uneven illumination over the surface of the crystal (discussed below) or with bad electrode contacts (confirming the results of others<sup>3</sup>). If a crack developed in the crystal near an electrode, the maximum was obtained. The occurrence of a maximum, whatever its cause, was always accompanied by the possibility of obtaining a back-photocurrent,  $I_b$ , *i.e.*, a current in the opposite direction

<sup>17</sup> Barth, *Z. Physik*, 1934, **87**, 399; Penick, *Rev. Sci. Instr.*, 1935, **6**, 115.

<sup>18</sup> Levy and Campbell, *J.*, 1939, 1442.

<sup>19</sup> Carswell and Iredale, *Austral. J. Appl. Sci.*, 1953, **4**, 329.

<sup>20</sup> Sangster and Irvine, *J. Chem. Phys.*, 1956, **24**, 670.

to the original, when the field was switched off or decreased and the crystal re-illuminated. This result<sup>21</sup> is ascribed to the build-up of space charge in the crystal. The measure of the back-photocurrent under uniform illumination indicated the quality of the electrode contacts. Fig. 1 shows  $I_s-t$  curves with bad electrode contacts and the effect of remaking a bad contact; other substances behave similarly.

When the light is switched off but the field remains on,  $I_s$  decays in two stages, an initial one where the decay is too fast to measure, and a slow final one, covering the last 10%, where the decay followed a first-order law with a constant  $k = 0.04 \text{ sec.}^{-1}$ . This slow stage only

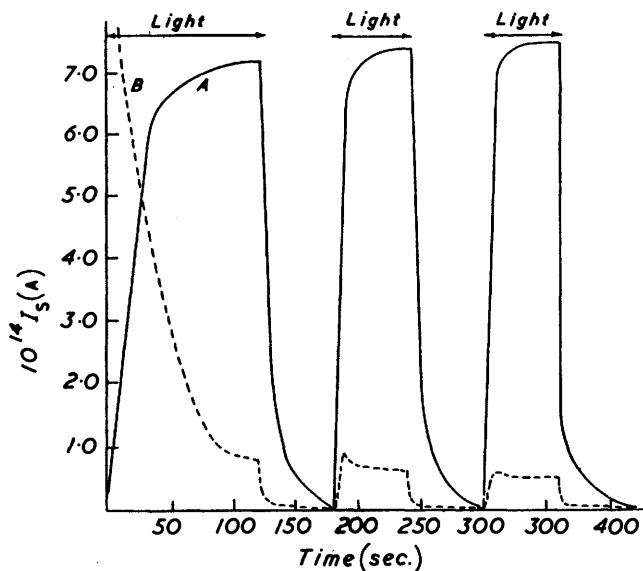
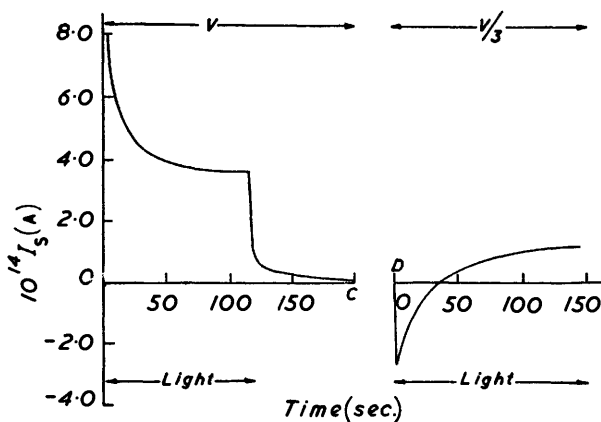


FIG. 1a. Effect of remaking a bad contact with an anthracene crystal ( $4 \text{ mm.} \times 2 \text{ mm.} \times 5 \mu$ ) at a field strength of  $500 \text{ v cm.}^{-1}$  and light intensity of  $10^{10} \text{ quanta sec.}^{-1} \text{ cm.}^{-2}$ . A, Good contact; B, bad contact.

FIG. 1b. Evidence of space charge in an anthracene crystal ( $5 \text{ mm.} \times 1 \text{ mm.} \times 4 \mu$ ) with bad contacts at a field strength of  $1000 \text{ v cm.}^{-1}$  and light intensity of  $10^{10} \text{ quanta sec.}^{-1} \text{ cm.}^{-2}$ .

Between C and D an interval of 7 min. was allowed for decay of capacitive coupling effects in the circuit caused by altering the potential.



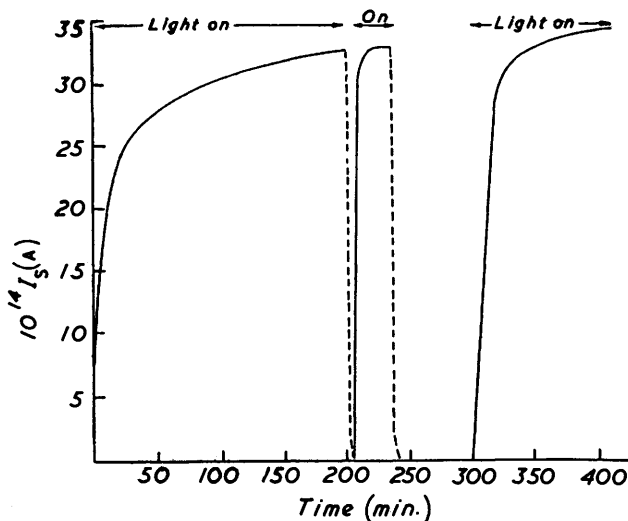
occurred when faulty electrode contacts were present, and the fact that it was due to faulty contacts was illustrated by deliberately introducing such faults, whereupon the decay from  $I_p$  to  $I_0$  followed first-order kinetics for about 30 sec. with a constant  $k_1 = 0.11 (\pm 0.02) \text{ sec.}^{-1}$ , and thereafter a first-order decay occurred with the same constant  $k_2 = 0.04 (\pm 0.01) \text{ sec.}^{-1}$ . Both  $k_1$  and  $k_2$  were independent of  $V$  (field strength),  $L$  (light intensity) and  $\lambda$  (wavelength).

The decay of  $I_b$  was also of the first order with a constant  $k_b = 0.06 (\pm 0.01) \text{ sec.}^{-1}$  at  $L = 10^{10} \text{ quanta sec.}^{-1} \text{ cm.}^{-2}$ ;  $k_b$  was independent of  $V$  and  $\lambda$  but increased as  $L$  increased. The production and the decay of the back-photocurrent  $I_b$  were studied as a function of  $\lambda$

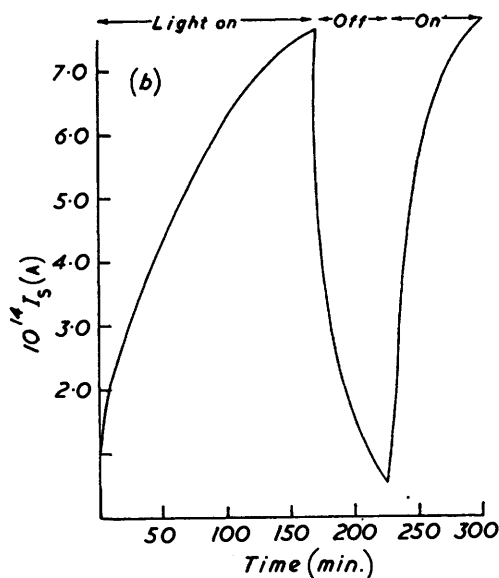
<sup>21</sup> Chynoweth and Schneider, *J. Chem. Phys.*, 1954, **22**, 1021.

(wavelength), all wavelengths in the absorption region being effective. Once the back-photo-current had been produced and allowed to decay completely, it could not be re-created, even by use of light of shorter wavelength. For example, if  $I_b$  was thus completely "eliminated" by light of  $\lambda$  4039 Å, then subsequent illumination at shorter wavelengths (e.g., 3650 Å) gave no

FIG. 2. Plot of surface current against time for a long interval.



(a) 1 : 2-5 : 6-Dibenzanthracene (crystal 1.5 mm.  $\times$  1 mm.  $\times$  2  $\mu$ ). Field strength 1000 v cm.<sup>-1</sup>, light intensity  $1.4 \times 10^{18}$  quanta sec.<sup>-1</sup> cm.<sup>-2</sup> at 3650 Å.

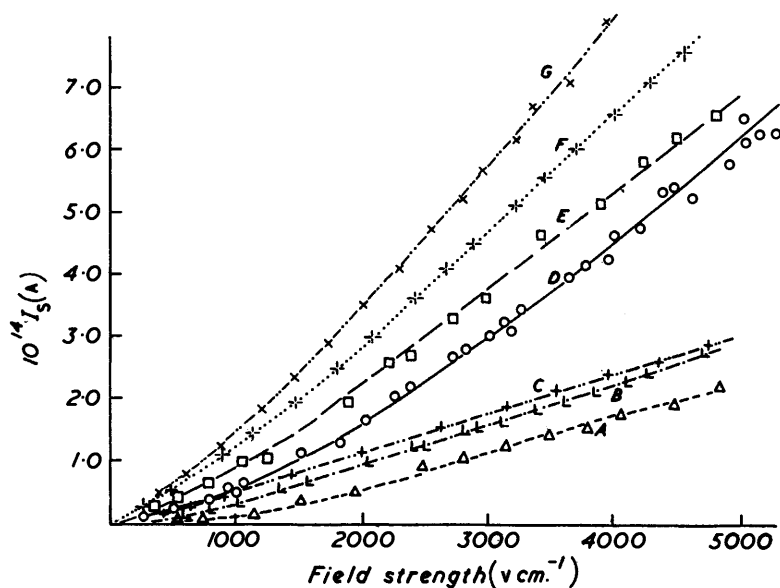


(b) Phenanthrene (crystal 3 mm.  $\times$  1 mm.  $\times$  1  $\mu$ ). Field strength 2000 v cm.<sup>-1</sup>, light intensity  $3 \times 10^{14}$  quanta sec.<sup>-1</sup> cm.<sup>-2</sup>, polychromatic at wavelengths greater than 3000 Å.

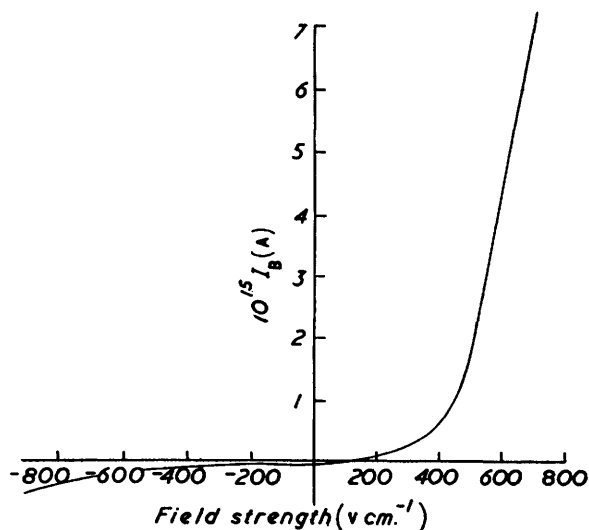
further  $I_b$ . This contrasts with a previous result,<sup>3</sup> but this is understandable if  $I_b$  in that case had not been completely eliminated in the first illumination. Irrespective of the wavelengths (4100—2600 Å) used to create the space-charge responsible for  $I_b$ , any wavelength in the same range was effective in eliminating it.

Over longer periods,  $I_s$  increased steadily with every substance (see Fig. 2). A similar

FIG. 3a. Surface current-field strength curves.



Crystal	Crystal size	Light intensity (quanta sec. <sup>-1</sup> cm. <sup>-2</sup> )
A <i>p</i> -Terphenyl .....	2 mm. × 1 mm.	$6 \times 10^{14}$
B Phenanthrene .....	2 mm. × 1 mm.	$4 \times 10^{12}$
C Naphthalene .....	5 mm. × 1 mm.	$4 \times 10^{13}$
D Chrysene .....	2 mm. × 1 mm.	$2 \times 10^{12}$
E Anthracene .....	4 mm. × 1 mm.	$2 \times 10^{10}$
F Pyrene .....	3 mm. × 1 mm.	$6 \times 10^{12}$
G 1:2-5:6-Dibenzanthracene ...	2 mm. × 1 mm.	$6 \times 10^{11}$

FIG. 3b. Bulk current-field strength curves for an anthracene crystal (10 mm. × 10 mm. × 5 mm.) with a light intensity of  $1.4 \times 10^{13}$  quanta sec.<sup>-1</sup> cm.<sup>-2</sup> on one electrode.

result has been observed with tetracene,<sup>1</sup> anthracene,<sup>21</sup> rhodamine B, and crystal-violet.<sup>14, 15</sup> When the light was switched off,  $I_S$  fell almost to zero rapidly (Fig. 2a), except with phenanthrene (Fig. 2b). Re-illumination within a short time (Fig. 1a) restored  $I_S$  to the value obtained just before switching off. A longer interval lengthened the time of the second build-up. Field-free illumination lowered the subsequent build-up time. It is important that if the field direction were reversed at any time of this build-up, the current was much smaller, but gradually increased, thus indicating that the electrodes were being polarized (double layer). Because of the gradual increase in  $I_S$  with time, a standard time of three minutes was used in the other experiments to be described.

With the sandwich cell, the peak current was always followed by a drop to a steady value. For a crystal 5 mm. thick, no back-photocurrent was detected with the positive electrode illuminated unless a very high light intensity was used. For a thin sublimation flake,  $I_b$  was about one-twentieth of  $I_c$  when the positive electrode was illuminated and about one-fifteenth when the negative electrode was illuminated. In such cases, the electrode contacts were deemed satisfactory.

*Current-Field Strength Relation.*—Some  $I_S$ - $V$  curves (where  $V$  is the ratio of applied voltage to electrode separation) in the literature show straight lines for tetracene and anthracene,<sup>1, 5, 21</sup> but other workers<sup>3, 4</sup> have found that, for anthracene, the curve bends towards the current axis with increasing voltage. After a very large number of surface-cell experiments on many crystals of each substance the results in Fig. 3 were established as representative. There is a slight upward trend most noticeable at comparatively low field strengths. In the case of *p*-terphenyl, the curvature was more pronounced. Experimental precautions observed included taking the points at the various voltages in a nearly random order (*e.g.*, for chrysene the order of points shown in Fig. 3a, with increasing field strength was 8, 4, 24, 9, 5, 25, 10, 6, 23, 11, 26, 22, 12, 27, 21, 3, 13, 20, 28, 7, 14, 19, 15, 29, 18, 2, 16, 30, 17, 1), reversing the direction of the field on each crystal and repeating the observations, and the use only of crystals in which  $I_b$  was negligible and the electrode contacts therefore satisfactory. Failure to observe the last precaution and to neutralize the resultant space charge produced curves which bent towards the voltage axis. The shape of the curves was independent of the polarization of the light (in the range of Table 1) and its intensity.

With a sandwich cell the direction of the field made a great difference to the plot of bulk current against field strength in agreement with previous work;<sup>3, 21</sup> see Fig. 3b.

The field direction in the (001) plane made no difference to the surface current, as was shown by experiments on the one crystal with four electrodes.

*Current-Light Intensity Relation.*—Plots of surface current against light intensity for four substances in the surface cell are shown in Fig. 4. The linear relation between  $I_S$  and  $L$  reported earlier for anthracene<sup>1, 21</sup> holds for light intensities less than  $1.6 \times 10^{13}$  quanta  $\text{sec}^{-1} \text{cm}^{-1}$ . The shape of the curves was independent of the polarization of the light, wavelength (in range of Table 1) and field strength. Goldsmith,<sup>4</sup> who varied  $L$  over a 100-fold range, reported a tendency to saturation, but this did not occur in our experiments over a wider range.

TABLE 1. Ratio of number of electrons in external circuit to number of quanta absorbed, at an applied voltage of 1 v  $\text{cm}^{-1}$  with uniform illumination in the surface cell.

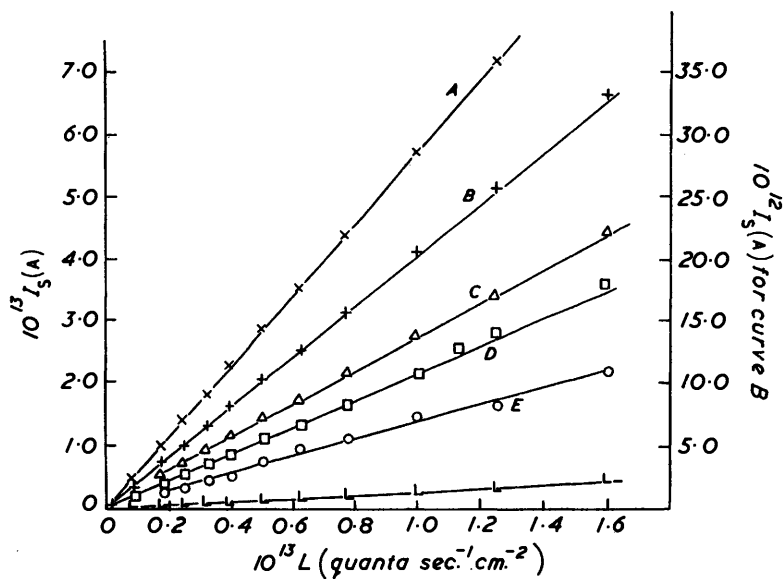
Crystal	Range (Å)	Ratio	Crystal	Range (Å)	Ratio
Anthracene .....	3300—3920	$10^{-7}$	Acridine .....	3500—4000	$10^{-9}$
1 : 2-5 : 6-Dibenzanthracene .....	3000—4000	$2 \times 10^{-8}$	Dibenzothiophen .....	3000—4000	$5 \times 10^{-10}$
1 : 2-Benzanthracene ...	3000—3800	$5 \times 10^{-9}$	Phenanthrene .....	2600—3130	$3 \times 10^{-10}$
Chrysene .....	3000—3650	$4 \times 10^{-9}$	Naphthalene .....	2600—3130	$5 \times 10^{-11}$
Pyrene .....	3000—3650	$10^{-9}$	<i>p</i> -Terphenyl .....	2600—3100	$3 \times 10^{-12}$
			Diphenyl .....	2600—2800	$10^{-12}$

The order of magnitude of the currents obtained with a known number of quanta may be seen from Table 1 where each result represents an average over the wavelength range stated.

The only ratio of current to quanta observed previously<sup>2</sup> (on anthracene,  $5 \times 10^{-7}$  electrons/quantum) was in reasonable agreement with the above.

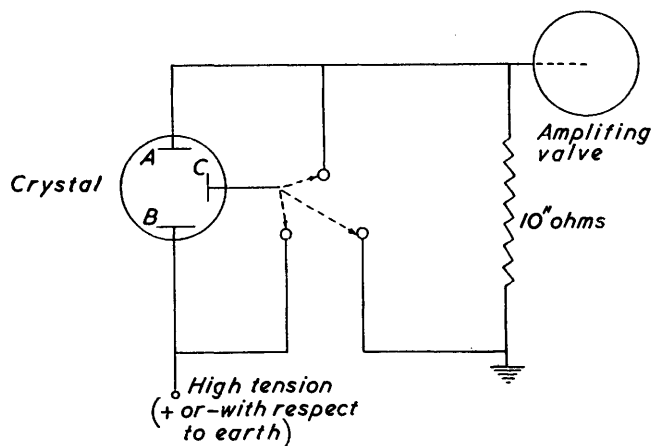
With the sandwich cell, the curve of bulk current against intensity depended on whether the illuminated electrode was positive or negative. When it was positive, the current was proportional to  $L$ , and when negative it was proportional to  $L^{\frac{1}{2}}$ .  $L$  was varied from zero to

FIG. 4. Surface current–light intensity curves.



Crystal	Crystal size	Field (v cm <sup>-1</sup> )
A Chrysene .....	3 mm. × 1 mm.	2300
B Anthracene .....	2 mm. × 2 mm.	500
C Pyrene .....	4 mm. × 1 mm.	4000
D 1:2-5:6-Dibenzanthracene ...	2 mm. × 1 mm.	500
E Pyrene .....	4 mm. × 1 mm.	2000
F Chrysene .....	3 mm. × 1 mm.	400

FIG. 5. Schematic diagram of bulk-current experiments.



A and B are electrodes on one face (001) of a thin ( $10\ \mu$ ) anthracene crystal, C is an Aquadag ring on the opposite face (001) of the crystal, but of such a diameter that A and B are within it. Direct connection was made between C and A, B, or earth. The light shines wholly within the ring.

$10^{13}$  quanta  $\text{sec}^{-1} \text{cm}^{-2}$  over a 200-fold range of applied voltage. For a comparable voltage and light intensity,  $I_B$  was estimated as about 1–10% of  $I_S$ .

The effect of variation of the area of illumination was studied for the surface cell. Before any experiment was begun the whole crystal was irradiated to render it free from space charges. After our irradiating the whole area between the electrodes, then switching off both the light and

TABLE 2. Photocurrents in anthracene single crystals.

Primary light (in applied field)	Secondary light (probe) (no applied field)	Current observed with secondary light (f, forward; b, back)
(1) Overall	Near either electrode	$I_b$ , small
(2) "	Central area	$I_b$ , smaller than in (1)
(3) Probe near either electrode	Central area	$I_f$
(4) " "	Same area as primary	$I_b$ , large
(5) " "	Near other electrode	$I_b$ , smaller than in (4)
(6) Probe in central area	Central area	$I_b$ , large
(7) " "	Near either electrode	$I_f$ , small

the field, and then reirradiating it,  $I_b$  was very small, about 1/50th of the original forward current. However, by using a light probe at various positions between the electrodes both an  $I_p$  and an  $I_b$  were obtained. The maximum current  $I_p$  was approximately constant for different

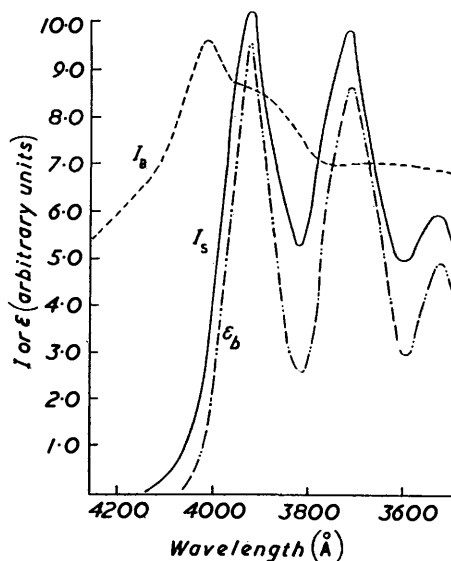


FIG. 6. Spectral dependence of  $I_B$  and  $I_S$  for anthracene compared with crystal absorption spectrum.

*b*-Polarisation; see Bree and Lyons, *J.*, 1956, 2662.

The current scale is different for each curve; readings at all wavelengths are relative to that of the first peak. The number of incident quanta is the same for all wavelengths.

$I_B$ , crystal 10 mm.  $\times$  10 mm.  $\times$  5 mm.; applied voltage 500 v.

$I_S$ , crystal 5 mm.  $\times$  2 mm.  $\times$  2  $\mu$ ; field 1000 v  $\text{cm}^{-1}$  with uniform illumination.

positions of the probe between the electrodes. A similar result was obtained if the two electrodes were on one (001) face of the crystal, well away from the edges, and a probe was moved across the opposite (001) face. When the probe moved beyond an electrode  $I_p$  decreased rapidly as did the steady current  $I_0$ . When the probe light fell on the face of the crystal which held the electrodes (the field being on throughout), switching the light off and then on again after only a short interval restored  $I$  to the steady value,  $I_0$ , less than  $I_p$ . If, however, the probe was moved before switching the light on again  $I$  reached a peak.

Other experiments where two electrodes were used are listed in Table 2. These show the conditions for obtaining a back current  $I_b$ , and also for obtaining a forward photocurrent,  $I_f$ , even in the absence of an applied field.

Experiments were performed with three electrodes of which two, *A* and *B*, were on one (001) face of an anthracene crystal and the third, *C*, a ring of about 4 mm. internal diameter, on the opposite (001) face. The light was incident on the ring side and fell only within the ring. Connections were made as in Fig. 5. The results are shown in Table 3. A current is indicated as negative when electrons flowed from earth to the grid of the valve. A large current was obtained only in the cases (iv) and (v) when *C* was at a potential considerably different from that of *A*. Consequently the experiments showed that current passes through the bulk of the



crystal and does not flow only along the surface. Since the current in (iv) was much larger than that in (v) there is additional evidence that the carriers are positive holes. Experiments

TABLE 3. Photocurrents with three electrodes, A, B, and C.

	(i)	(ii)	(iii)	(iv)	(v)
Potential of B (v) .....	450	-450	+450	220	-220
Potential of C (v) .....	0	0	floating	220	-220
I (arbitrary units) .....	-10	-7	+60	+8000	-300

with a guard ring were made with sandwich cells; it was shown again that a current actually passed through the bulk of the crystal and did not need to pass along the surface.

*Current-Wavelength Relation.*—With the surface cell, the spectral dependence of  $I_S$  is described in general by a curve which resembles the absorption spectrum, varying with the polarization of the light in a way which is semiquantitatively similar. These results will be discussed fully in a later paper.

With the sandwich cell the close similarity of the spectral-dependence curve to the absorption spectrum was lost (see Fig. 6). The chief features observed with the sandwich cell are the loss of structure in the spectral dependence curve (only one maximum was obtained, somewhat displaced towards the red from the first maximum found with the surface cell), and the presence of an appreciable current at wavelengths towards the red end of the absorption system.

### DISCUSSION

Most of the previous work on anthracene has been concerned with the surface currents. It is now clear that both surface and bulk currents occur and the dependence of the current upon, *e.g.*, wavelength, field strength, and surrounding gas is different in the two cases.

*Processes occurring.*—An overall picture of the processes thought to occur is as follows. When light is absorbed by the crystal some is re-emitted as fluorescence, some is thermally degraded, and a small fraction liberates current carriers, of which positive holes have the greater mobility. Both electrons and holes may be trapped. A rise in temperature lowers the trapping probability and so the photocurrent has a positive temperature coefficient. Space charges occur at the electrodes and, if the light falls on a limited area, also over this illuminated area. These are due to trapped carriers. Also, in the surface layers, a double layer of charge is assumed in order to explain the properties of surface currents such as carrier mobility, which is greater in the surface than in the bulk. Variation in the gaseous atmosphere may affect both the double layer and the production of carriers at the surface.

In the bulk the current is carried predominantly by positive holes<sup>22,21,4</sup> even when monochromatic light of relatively low wavelength (2240 Å) is used. It may be supposed that electrons have a smaller mobility than the holes in order to explain that  $I_+ > I_-$  (where  $I_+$  and  $I_-$  are the currents carried by positive holes and electrons respectively). The reason for this may well be that the positive electron affinity of anthracene molecules<sup>23</sup> results in a high probability of trapping at each molecular site. In addition, it is possible that an absorbed gas such as oxygen may act as an electron trap. The ion  $O_2^-$  is known to exist both in the free state and in crystals, but there is no evidence yet as to just how the electron is held on the crystal surface. In the surface cell also  $I_+ > I_-$ , but the values are much more similar than those in the bulk, indicating that the electrons carry a greater fraction of  $I_S$  than of  $I_B$ .

When light is absorbed, migration of energy is known to occur<sup>24</sup> and any quantum will make about  $10^5$  hops to neighbouring centres before fluorescence occurs. The probability of a transition to an ionized state must be very much less than the probability of fluorescence, in view of the fact that the occurrence of photoconduction leaves the fluorescence yield (about 0.9) unchanged. A low probability of ionization is consistent with the estimated

<sup>22</sup> Putseiko, *Doklady Akad. Nauk S.S.S.R.*, 1949, **67**, 1009.

<sup>23</sup> Lyons, *Nature*, 1950, **163**, 193.

<sup>24</sup> Bowen, Mikiewicz, and Smith, *Proc. Phys. Soc.*, 1949, *A*, **62**, 26; Simpson, *Proc. Roy. Soc.*, 1957, *A*, **238**, 402; Dexter, *J. Chem. Phys.*, 1953, **21**, 836; Ferguson, *Austral. J. Chem.*, 1956, **9**, 172.

quantum efficiency of carrier liberation. Although carrier liberation scarcely affects fluorescence, it is possible that it is comparable in efficiency with the thermal degradation of the absorbed energy. Recombination of positive holes with electrons, possibly with the occurrence of fluorescence, is also expected to occur. Consequently, not all the carriers liberated will reach the outer circuit.

*Surface Current.*—For  $I_s$ , many of the results are summarized for a given electrode separation and for uniform illumination by monochromatic light, by the relation

$$I_s \propto \epsilon [\text{O}_2]_{\text{ads.}} \cdot vL^n \exp(-2300/T) \cdot f(t) \quad (1)$$

where  $\epsilon$  is the extinction coefficient,  $[\text{O}_2]_{\text{ads.}}$  the surface concentration of adsorbed oxygen,  $v$  the applied voltage,  $L$  the total light intensity incident on the crystal,  $n$  a number between 0.5 and 1.0 (often 1.0),  $T$  the absolute temperature, and  $f(t)$  a function of the time of illumination. The dependence of  $I_s$  upon  $\epsilon$ ,  $[\text{O}_2]_{\text{ads.}}$ , and  $T$  is discussed elsewhere.<sup>7,25</sup> The relation (1) is to be regarded as approximately correct over a wide range of the variables. Some deviations will be mentioned below.

The actual process by which carriers are produced appears to be limited to three possibilities. The excited crystal level may undergo a transition directly to an ionized state or else ionization may be induced by the presence of an electric field<sup>26</sup> or of a molecule such as  $\text{O}_2$ . There are various fields present in the crystal, as well as the applied field which has been suggested<sup>10</sup> as responsible, namely (a) the local field surrounding an ion already produced, which at the nearest-neighbour distance is expected to be of the order of  $10^7$  v cm.<sup>-1</sup> and to fall off to about 200 v cm.<sup>-1</sup> at about 1000 Å distance; (b) the field near the surface which may act as a part of a diffuse double layer<sup>27,6</sup> [this is related to (a) since charges may be trapped in the surface layer]; and (c) space-charge fields already mentioned, also built-up from fields of type (a). Any field present would of course have some effect. The various transition probabilities are not known. For light absorbed near a surface, (b) is likely to be important and may play a part in explaining the spectral dependence of  $I_s$ , along somewhat similar lines to those previously suggested.<sup>28</sup> However, for ionization in the interior of the crystal (b) will not be relevant. Since  $I_s$  is decreased by removal of the oxygen in the surrounding atmosphere it was previously postulated<sup>7</sup> that some oxygen-anthracene compound was an intermediate in the production of current carriers. Nitric oxide, sulphur dioxide, and other gases behave similarly to oxygen,<sup>6,7</sup> but whilst compounds are definitely formed<sup>7</sup> with oxygen, nitric oxide, and sulphur dioxide, it is possible that these have nothing to do with carrier liberation. The effect of gases on the photocurrent now seems more likely<sup>6</sup> to be by way of a double-layer effect either on the efficiency of carrier production or on the mobility of carriers when formed or else on both the production and the mobility.

Double layers of charges occur generally at phase boundaries, and so may be expected at the crystal-gas (or crystal-vacuum) interface. The idea of a double layer can be used to interpret the result shown in Fig. 2. The build-up time of  $I_s$  was decreased by prior illumination in the absence of a field. On the assumption that light by itself does not give rise to space-charge effects at the electrodes, it is possible to conclude that in air the light liberates charges in the surface layers and these then alter the charge distribution in the double layer. Eventually, if the double-layer distribution becomes nearly constant, then  $I_s$  should become steady, as is observed.

Space charges near the electrodes, even if not produced by uniform illumination of the crystal, are certainly present whenever a field is present, and decay when the field is switched off. Evidence for electrode space charges is seen in the fact that reversal of the applied voltage caused a temporary diminution in  $I_s$ , which gradually returned to its

<sup>25</sup> Bree and Lyons, unpublished work.

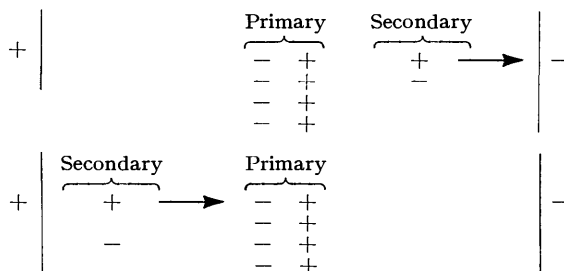
<sup>26</sup> Zener, *Proc. Roy. Soc.*, 1934, **145**, A, 523.

<sup>27</sup> Bardeen, *Phys. Rev.*, 1947, **71**, 717.

<sup>28</sup> Lyons, *J. Chem. Phys.*, 1955, **23**, 220.

original value. The use of alternating fields is essential to eliminate such effects. Electrode space charges account for the result of experiment (5) in Table 2. The electrode space-charge field is smaller than the field due to space charges produced by a light probe in a neighbouring area; this is seen from experiment (7) in Table 2, because the secondary light produced a forward and not a back current. Non-uniform illumination [experiments (4), (5), and (6) of Table 2] shows clearly how the light produces a space-charge field which is predominantly situated in the area of the light beam and largely remains during the interval before the secondary illumination. This we explain by the trapping of the electrons near the place of their formation whilst the positive holes move in the field a certain distance (small in comparison with the size of the light spot) but cannot easily escape from the region of negative charge. When trapped, the holes set up with the electrons a reverse space-charge field and further movement of holes is randomly directed. Trapped electrons constitute a likely trap for positive holes. Different trap-depths would be given by different distances of separation of the positive and negative centres. Recombination of holes with electrons takes place in the dark but is assisted by re-illumination (secondary light). In this way experiment (6) of Table 2 is explained. It does not follow that the secondary light produces recombination of only those holes and electrons formed by the primary. More charges will be produced by the secondary light and the electrons freed by the primary light may combine with secondary holes and *vice versa*. On this view,  $I_b$  is not caused by the "de-trapping" of electrons and holes. In the secondary light all wavelengths were equally effective, and evidence of different trap depths was found in such experiments. From experiments (7) and (3) it is seen that the charge separation produced by the primary light may be neutralized as a result of the secondary light on a different area, the charges flowing in the forward sense, indicated in positive holes by the arrows in Fig. 7. For experiments (1) and (2) the small value of  $I_b$  shows that a small space-charge field is situated near the electrodes.

FIG. 7. Schematic diagram showing how  $I_1$  and  $I_b$  arise from secondary illumination because of space-charge fields due to the primary light (cf. Table 2).



An ingenious experiment by Goldsmith<sup>4</sup> may be interpreted on a similar basis. He applied simultaneously a uniform background illumination of variable intensity over all the crystal and a probe light-spot of constant intensity. The currents due to the probe were found to increase to a maximum with increasing intensity of background light. It was concluded that the background light liberated carriers from a certain class of trap. We now suggest that the function of the background was to produce charges over the entire area of the crystal so that no space-charge field could be built up by the probe light. From the experiment it is seen that the probe space charge became negligible when the background light produced a current about four times as great as that due to the probe light. In other words, the carriers produced by the background light were sufficiently numerous to neutralize any charges from the probe which otherwise would have given rise to a space-charge field. This explanation does not contradict Goldsmith's, but is rather an amplification of it.

*Current-Field Relation.*—Surface current-field strength curves are nearly linear and this justifies the use of a relation such as  $I_S = p\mu_S F$ , where  $p$  is the number of carriers,  $\mu_S$  their average mobility in the surface layers,  $F$  the field, assumed nearly equal to the applied voltage/cm. Deviations from linearity may be due to the presence of space charges at the electrodes, which are not proportional to  $V$ . Evidence for this is that  $I_b$  (relative to the forward current) is larger at lower values of  $V$ . They may also be due to the variation of the field in a direction,  $\epsilon$ , perpendicular to the surface. Both  $p$  and  $\mu_S$  are expected to depend on  $z$ . Consequently the accurate expression for  $I_S$  will be complicated and deviations from linearity between  $I_S$  and  $V$  therefore expected. A further cause of deviation may be the necessity of a field for the production of some of the current carriers. However, this has not been established. Bad electrode contacts gave deviations from linearity in the opposite sense to that shown in Fig. 3(a).

The values of  $p$  and  $\mu_S$  must be derived from conduction measurements since no Hall-effect measurements have been reported for hydrocarbons. Since  $I_S$  was proportional to  $L$ , in the range considered, the relation  $I_S = p\mu_S F$  is further substantiated provided that  $p \propto L$ . This is true even when  $p$  is taken to include both electrons and positive holes. It may be inferred, furthermore, that the recombination of carriers follows first-order kinetics. Since the decay of  $I_S$  when the light is switched off is of first-order, this decay process may be attributed to recombination of carriers.

The mobility can be estimated in several ways. Some values obtained previously and also some new ones are shown in Table 4. If  $b$  is disregarded because it applies to a film and not to a single crystal, and the other values are assumed to be comparable, then  $5 \times 10^{-3} < \mu < 10^3 \text{ cm.}^2 \text{ v}^{-1} \text{ sec.}^{-1}$ . However, since  $a$ ,  $c$ , and  $d$  presumably refer to  $\mu_B$

TABLE 4. *Mobilities (cm.<sup>2</sup> v<sup>-1</sup> sec.<sup>-1</sup>) in anthracene.*

No.	Value	Ref.	Method
<i>a</i>	$10^{-2}$	11, 29	Semiconduction of single crystals, the number of molecules able to yield carriers being assumed to be $10^{21} \text{ cm.}^{-3}$ .
<i>b</i>	$10^{-4.1}$	10	As for <i>a</i> , but with use of other values for the activation energy (0.96 ev) and conductivity of films.
<i>c</i>	1.0	21	Mean free path, $\lambda_c$ (estimated as $10^{-4} \text{ cm.}$ from the saturation of $I_B$ with $F$ when the negative electrode of a sandwich cell was illuminated), and the carrier life-time $\tau$ (estimated as $5 \times 10^{-8} \text{ sec.}$ by comparison with life-times obtained in certain inorganic crystals having a high trap density) through $\lambda_c = \mu\tau F$ .
<i>d</i>	$5 \times 10^{-3}$	4	As <i>c</i> , with an experimental value for $\tau$ .
<i>e</i>	$10^2$	4	From the range of the carriers (calc. as 0.1 cm. from the field distribution on a crystal surface determined by light-probe expts.) and $\tau$ (taken as $10^{-5} \text{ sec.}$ ) through $\text{Range} = \mu\tau F$ (cf. <i>c</i> and <i>d</i> ).
	$10^{-2}/Q$	—	$Q$ is the ratio of carriers produced to quanta absorbed; it is likely to be less than unity for any hydrocarbon and $< 0.1$ for anthracene which has a high fluorescence yield. [ $\mu$ was taken as $I_S/(LQ\tau F)$ ; $I_S/(LF)$ is given in Table 1 and $\tau$ was taken as $10^{-5} \text{ sec.}$ ] This gives the value $\mu = 10^{-2}/0.1 = 10^{-1}$ .
<i>g</i>	<i>ca.</i> $10^3$	—	By assuming that the drift mobility is related to the thermal velocity $u$ ( $10^7 \text{ cm. sec.}^{-1}$ ) of an electron by $\mu = u \exp(-E_T/kT)$ , where $E_T$ is the depth of the trap below the conduction band, and was assumed to be measured by the temperature coefficient of $I_S$ which is $^{25} 0.2 \text{ ev.}$

for the crystal bulk and  $e$ ,  $f$ , and  $g$  to  $\mu_S$ , for the surface layers, it may tentatively be concluded that  $10^{-3} < \mu_B < 1$  and  $10^{-1} < \mu_S < \text{ca. } 10^3$ .

Photo-experiments on the bulk crystal usually give space-charge effects which lower the value of  $I_B$  and therefore restrict us to semiconduction measurements to obtain  $\mu_B$ . The value of  $\mu_B$ ,  $10^{-2}$ , for single crystals<sup>29</sup> (in the 001 plane) assumes that anthracene is an intrinsic semiconductor, a conclusion which is compatible with the correlation of the activation energy of conduction with a molecular property.<sup>31, 10</sup>

<sup>29</sup> Mette and Pick, *Z. Physik*, 1953, **134**, 566.

<sup>30</sup> Shockley, "Electrons and Holes in Semiconductors" (van Nostrand, N.Y., 1950), p. 240.

<sup>31</sup> Carswell, Ferguson, and Lyons, *Nature*, 1954, **173**, 736.

If  $\mu_S$  is taken as  $10^3$  and since  $\tau = 10^{-5}$ ,  $L = 10^{13}$  and  $Q = I_S/(\mu L \tau F)$ , then  $Q = 10^{-5}$ . The assumption that  $Q < 10^{-1}$  (as seems probable) leads to a value of  $\mu_S$  greater than  $10^{-1}$  which is again consistent with  $\mu_S$  being greater than  $\mu_B$ .

*Bulk Current.*— $I_B$  is smaller than  $I_S$  owing both to the space charge and lower mobility in the bulk. The existence of space charge accounts for the  $I_B-t$  curve which shows the typical drop from a peak to a steady value.

*Current-Voltage Curves.*— $I_B-V$  curves [Fig. 3(b)] are markedly non-linear. This is explained by the build-up of space charge. No current saturation was obtained upon increasing the voltage when the light fell on the negative electrode, although the current increased only slightly. The  $I_B-V$  curve differed according to the electrode illuminated. This difference is the basis of determining the sign of the carriers.

*Current-Light Intensity Curves.*— $I_B-L^n$  curves gave  $n$  different from unity (about 0.5) only in the case when the negative electrode was illuminated. This was due to either a bimolecular process of carrier removal or else a distribution of traps above the Fermi limit of the type described elsewhere.<sup>32</sup> The charge distribution in the crystal should depend on which electrode was illuminated since the mobilities of electrons and positive holes are different. Different distributions of charges are assumed to give rise to different kinetics of carrier removal.

*Spectral Dependence.*—The difference in the spectral dependence of  $I_B$  and  $I_S$  may be associated with the greater distance of penetration of the light at wavelengths above 4100 Å. The greater the penetration the less will the carriers produced be affected by the surface layers. In accordance with this view,  $I_B$  is altered much less than  $I_S$  by the surrounding atmosphere. The existence of a current above 4100 Å indicates a small positive extinction coefficient of the crystal. Such small values of  $\epsilon$  have not yet been measured. At low temperatures the Boltzmann bands of the absorption spectrum disappear and consequently the long-wavelength tail of the spectral-dependence curve should also disappear. This experiment would therefore provide a test of the explanation just given.

The substances other than anthracene which were examined differed only in the magnitudes of the currents obtained. Both the production and the mobility of carriers are likely to be different in each case. The order of arrangement of the compounds in Table I is closely similar to the order of arrangement by a number of molecular properties, *viz.*, the energies of transition to the first excited singlet and triplet levels, the molecular-ionization energy, the molecular electron affinity, the maximum free valency in the molecule, the minimum atom localization energy and the radical affinity. The ease of aerial oxidation of the molecules may also be correlated. Which of the molecular properties is most significant will be considered elsewhere.

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<sup>32</sup> Rose, *R.C.A. Revs.*, 1951, **12**, 362.