

stabilizers. Normal operating conditions were employed. The samples were degassed and sealed, under vacuum in Pyrex tubes of ca. 5 mm. o.d., with ca. 2% of tetramethylsilane (TMS) as internal reference and a 1 mm. capillary tube containing degassed benzene as external reference (ethylene sulfite was dissolved in a $\text{CCl}_4\text{-CHCl}_3$ mixture). The position of the center of each multiplet in the spectra is reported in parts per million (± 0.01) on the scale in which internal TMS is at 10 p.p.m., or 400 c.p.s. at 40 Mc.p.s.⁷ The internal TMS in ethylene sulfite solution is 263.0 c.p.s. removed from the external benzene. No corrections were applied for differences in bulk magnetic susceptibility of the sulfites and benzene.

The infrared spectra were recorded in conventional fashion on a Beckman IR-4 instrument equipped with sodium chloride and cesium bromide optics. The bands common to the two propylene sulfite isomers were in cm^{-1} : ca. 2975m, ca. 1460m, 1393m, 1212s, ($\nu \text{ S=O}$), 1057m, 909w, 834s, 680m and 382m. The bands which were different were for isomer i: 1333w, 1110w, 968s, 723m, 466m and 444m; and for isomer ii: 1140w, 1103w, 980m, 952m, 736m, 710w, 505m, 487m and 415m (s = strong, m = medium, w = weak intensity). These data are in reasonable agreement with those infrared bands for a propylene sulfite mixture which have been recorded previously.⁸

Dipole Moment.—The dielectric constants of dilute solutions of ethylene sulfite in benzene (ϵ) were measured at 25° over the weight fraction (ω) range of 0 to 0.1, using a Wissenschaftlich-Technische Werkstätten Dipolemeter, type

DM 01 operating at a frequency of 2 Mc.p.s. The linear expression relating ϵ and ω , derived by the method of least squares, was $\epsilon = 2.25 + \alpha\omega$, where $\alpha = 13.96$. By conventional methods, the following expressions relating ω with the specific volume (v) and refractive index (n) of the solutions at 25° were found: $v = 1.1445 + \beta\omega$, where $\beta = -0.469$ and $n = 1.4977 + \gamma\omega$, where $\gamma = -0.0304$. The value 3.74 was calculated for the electric moment (μ) of ethylene sulfite by substitution of the derived parameters α , β and γ in the equation of Everard, Hill and Sutton⁹ (M = mol.wt.)

$$10^4\mu^2 = M(92.0\alpha + 1.5\beta - 279\gamma + 1.7)$$

Benzene was of analytical grade redistilled under nitrogen. Contact of the solutions with the atmosphere was avoided as far as possible.

Acknowledgments.—The authors wish to record their appreciation of technical help on this project by Miss J. S. Hartman and Mr. J. J. Burke. The 60 Mc.p.s. spectra were obtained by Dr. C. Naar-Colin and the dipole moment measurement was carried out by Dr. C. H. Ruof. The authors also wish to thank Dr. A. A. Bothner-By for encouraging and helpful discussions.

(34) K. B. Everard, R. A. W. Hill and I. E. Sutton. *Trans. Faraday Soc.*, **46**, 417 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

Electrical and Magnetic Properties of Organic Molecular Solids. III. Violanthrene and Some Other Donors with the Acceptors *o*-Chloranil, Iodine and Tetracyanoethylene¹

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RECEIVED OCTOBER 31, 1960

A study of the electrical and magnetic properties (and how they are affected by illumination) of violanthrene as a donor matrix with a variety of acceptor layers is reported. The principal acceptor most thoroughly studied was *o*-chloranil. A reciprocal study also was made with *o*-chloranil as an acceptor matrix and phthalocyanine as donor in a laminated configuration. Kinetics of photo-induced transients, both in terms of conductivity and magnetic response, are reported. All of the results may be interpreted in terms of the transfer of electrons from the donor to the acceptor layer, giving rise to an orbital and electrostatically determined positive and negative ion and radical distribution on either side of the interface, respectively.

Introduction

Both the development of our knowledge of the electrical and magnetic properties of organic molecular electron donor-acceptor complexes²⁻⁴ and the development of concepts for the function of such complexes in biological energy transformations, including photosynthesis⁵ and muscle contraction,⁶ have prompted a further investigation of a configuration of molecules more closely resembling the lamellar systems of biology.^{7b, 8a} We report here an investigation of the electrical,

photoelectric, magnetic, photomagnetic and spectroscopic behavior of a variety of donor-acceptor systems in the laminated solid arrangement, that is, a donor layer in contact with an acceptor layer and a boundary established between them. A fundamental hypothesis underlying this work and deriving some support from it is: While the absorption of light in the charge transfer band by a donor-acceptor molecular complex in solution (or in the gas phase) might very well lead to the "effective" transfer of an electron from one of the components to the other, energy conversion or storage cannot be achieved in this way beyond that comprising an ordinary excited electronic molecular state. The return to the ground state (by emission or thermal decay) is too easy and rapid. If, however, the donor and acceptor components are each part of a solid and probably ordered array, charge separation may occur following the charge transfer act (resulting from light absorption) by a process of electron and/or hole migration with concomitant "trapping" in the two respective phases. Thus, the oxidized and reduced sites are not only long lived but widely separated so that relatively

(1) The work described in this paper was sponsored by the U. S. Atomic Energy Commission.

(2) (a) G. Tollin, D. R. Kearns and M. Calvin, *J. Chem. Phys.*, **32**, 1013 (1960); (b) D. R. Kearns, G. Tollin and M. Calvin, *ibid.*, **32**, 1020 (1960).

(3) (a) H. Akamatsu, H. Inokuchi and Y. Matsunaga, *Bull. Chem. Soc. Japan*, **29**, 213 (1956); (b) Y. Matsunaga, *ibid.*, **28**, 475 (1955), and *J. Chem. Phys.*, **30**, 855 (1959).

(4) See proceedings of conference on "Electronic Conductivity in Organic Solids," Duke University, April, 1960; to be published by Interscience Publishing Co., New York, N. Y., 1961.

(5) (a) Melvin Calvin, *Rev. Mod. Phys.*, **31**, 147 (1959); **31**, 157 (1959); (b) W. Arnold and R. K. Clayton, *Proc. Natl. Acad. Sci. U. S.*, **46**, 749 (1960).

(6) A. Szent-Gyorgyi, *Radiation Research Suppl.*, **2**, 4 (1960).

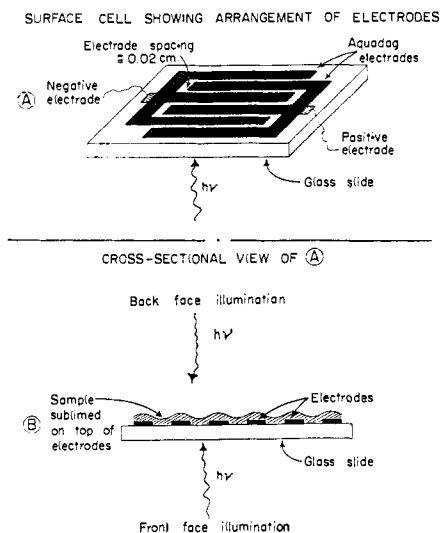


Fig. 1.—Schematic diagram of a surface cell used for most of the electrical measurements. The effective length of the electrodes in the typical surface cell was 15 cm. with a 0.02 cm. gap between the two electrodes.

independent chemical or electrical functions may be performed by them. Some experimental and theoretical basis for this is adduced in the Discussion.

II. Violanthrene Systems

Conductivity Measurements.—Unless otherwise specified, all of the conductivity measurements were made using violanthrene surface cells described earlier^{2a} and shown in Fig. 1. Pure violanthrene (see Fig. 2) was applied to the cell electrodes by vacuum sublimation and the exposed surface of violanthrene could then be treated with the proper electron acceptor (doping agent). A very important aspect of this type of cell construction is that the doping agent is separated from the measuring electrodes by a relatively thick layer ($\sim 5 \times 10^{-4}$ cm.) of violanthrene. The three electron acceptors used were *o*-chloranil, iodine and tetracyanoethylene. These were usually dissolved in benzene and then sprayed onto the exposed surface of the violanthrene surface cell. Application of iodine or *o*-chloranil to the violanthrene film by sublimation produced essentially the same changes in the properties of the violanthrene film as did the spray technique and therefore the latter method was used since it allowed greater control over the amount of material applied to a film.

The violanthrene⁷ used for the preparation of the conductivity cells was purified by vacuum sublimation in a muffle furnace. The *o*-chloranil and tetracyanoethylene were used as obtained. Resublimed reagent grade iodine was used without further purification.

In the measurements described below, 90 volts was applied to the sample cell and the cell conductivity was measured with apparatus described elsewhere.^{2a} Photocurrent was taken to be the difference between the current passing through the cell in the dark and the current passing through the cell during illumination. The cell could be illuminated either through the electrodes, referred to as front face illumination, or at the exposed surface of the violanthrene (surface away from the electrodes), referred to as back face illumination (see Fig. 1b).

Dark Conductivity. A. Variation with the Amount of Electron Acceptor Added.—Various amounts of the three electron acceptors *o*-chloranil, iodine and tetracyanoethylene were added to different violanthrene surface cells (each containing 10^{-6} – 10^{-5} mole of violanthrene⁸).

(7) Gift of Jackson Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours and Co., Wilmington, Del.

(8) The addition of *o*-chloranil to surface cells of phthalocyanine varying in thickness between 10^{-4} and 10^{-3} cm. produced the same enhancement of conductivity ($\times 10^3$).⁹ Therefore in this range of

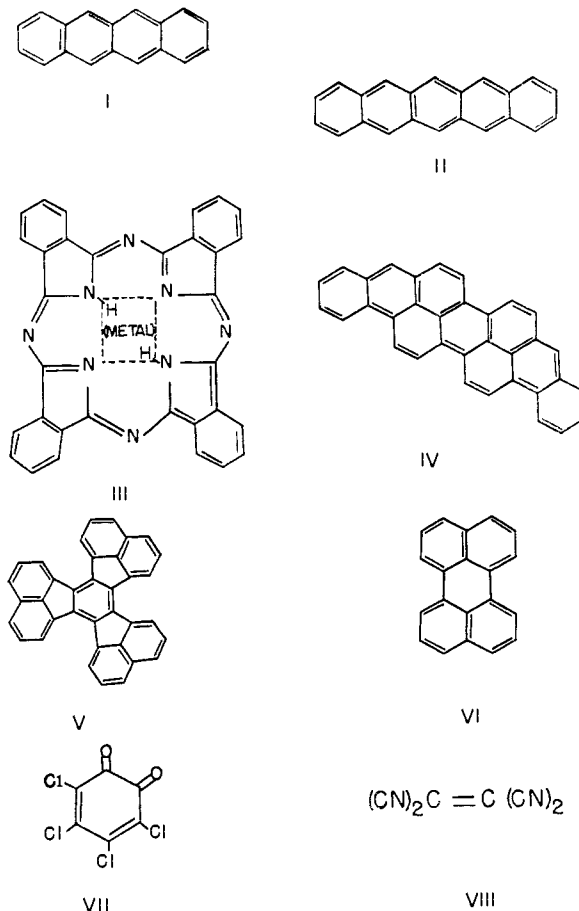


Fig. 2.—Structural formulas of the compounds studied: I, tetracene; II, pentacene; III, metal or metal-free phthalocyanine; IV, violanthrene; V, decacycene; VI, perylene; VII, *o*-chloranil; VIII, tetracyanoethylene.

Since the effect of these electron acceptors on the violanthrene dark conductivity was qualitatively the same (*i.e.*, the shapes of the conductivity vs. "doping" curves were the same), only the results of the violanthrene-*o*-chloranil system will be presented in detail. The variation of the dark current passing through a violanthrene surface cell with the amount of added *o*-chloranil is shown in Fig. 3. Quite similar curves were obtained for the violanthrene-iodine system and the violanthrene-tetracyanoethylene system. It is evident from this curve that the addition of 3.5×10^{-6} mole of *o*-chloranil causes the dark conductivity to increase by a factor of 8×10^3 over that of the pure film. The same amount of iodine was found to produce a 4×10^5 fold increase, while this amount of tetracyanoethylene produced only a 4×10^3 fold increase in the dark conductivity. The variation of the curves with different electron acceptors is largely in the region at which saturation sets in.

When 6×10^{-5} mole of *o*-chloranil was applied to a violanthrene surface cell, approximately 10^{-3} amp. could be drawn through the cell by the application of 90 v. If the large dark currents observed in this system were due to ionic conduction, then 10^{-3} amp. passing for about two hours would be sufficient to remove 6×10^{-5} mole of ions. The fact that 10^{-3} amp. may be passed for days through *o*-chloranil-doped violanthrene cells without an increase in the cell resistivity is clear evidence that at least in this case the conduction must be electronic rather than ionic.

Akamatsu, *et al.*,^{3a} have already performed this experiment with a solid complex of iodine-violanthrene and have reached the conclusion that conduction must be electronic

matrix thickness, the acceptor effect is exerted through the entire thickness of the cell.

(9) D. R. Kearns and M. Calvin, *J. Chem. Phys.*, June, (1961).

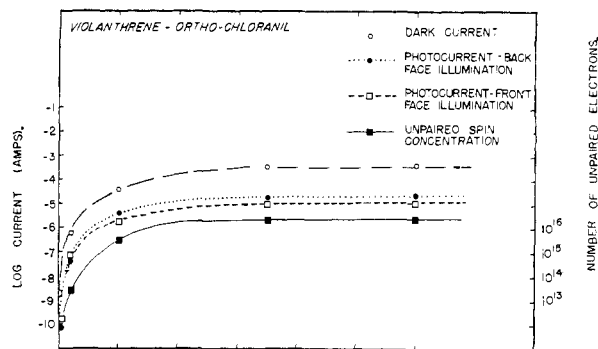


Fig. 3.—Variation of violanthrene dark current, photocurrent and unpaired spin concentration with the total amount of *o*-chloranil added to the surface cell holding $\sim 10^{-5}$ mole of violanthrene.

and not ionic. Our iodine-violanthrene surface cell was not stable over long periods of time so that the same experiment was not possible with this system. Akamatsu, *et al.*,^{3a} report that the substitution reaction of iodine does not take place with violanthrene so that the instability of our iodine-violanthrene system is probably due to evaporation of iodine off the violanthrene surface.

The resistance of a violanthrene cell doped with 3×10^{-5} mole of tetracyanoethylene was not found to increase after a current 4×10^{-5} amp. had passed through the cell for several days. Again, we conclude that the conduction must be electronic rather than ionic.

B. Temperature Dependence.—Inokuchi¹⁰ has found the temperature dependence for the dark current I , of pure violanthrene

$$I = I_0 e^{-\Delta\epsilon/kT}, \text{ with } \Delta\epsilon = 0.85 \text{ e.v.} \quad (1)$$

We found a similar logarithmic temperature dependence of dark conductivity for the doped violanthrene surface cells with $\Delta\epsilon = 0.2$ e.v. for *o*-chloranil, 0.25 e.v. for iodine-doped violanthrene. Akamatsu, *et al.*,^{3a} already have studied the electrical properties of the violanthrene-iodine system using a sandwich cell arrangement and found $\Delta\epsilon$ to be 0.07 e.v. The iodine surface cell is particularly unsuited for a study of the temperature dependence of the conductivity so it is not certain that the differences between the activation energies which we measured and those measured by Akamatsu are significant, particularly in view of the differences in geometry.

Photoconductivity. A. Variation with the Amount of Electron Acceptors Added.—The variation of the steady state photoconductivity with the amount of electron acceptor added was studied and the results for the *o*-chloranil-violanthrene system are shown in Fig. 3. Results obtained with the iodine-violanthrene and tetracyanoethylene-violanthrene system were again qualitatively the same. In all three cases it was found that doping enhances the photocurrent produced by back face illumination more than that for front face illumination.

Another factor of importance was that the increases in both the dark and the photoconductivity occurred rapidly (~ 30 sec. or faster) after doping, in all three cases; 5×10^{-5} mole of either *o*-chloranil or iodine when added to a violanthrene surface cell produced about a 10^3 -fold increase in photocurrent while a similar amount of tetracyanoethylene produced only a 10^2 -fold increase in the photocurrent.

B. Temperature Dependence.—The temperature dependence of the steady state photocurrent was measured only for the violanthrene-*o*-chloranil system. It had the same functional dependence as did the dark current (see eq. 1) with an activation energy of 0.2 e.v. No data were taken for the temperature dependence of the photocurrent in the iodine- or tetracyanoethylene-violanthrene systems.

C. Kinetics.—Following illumination, the photocurrent decreased to zero and in all three cases the current decayed exponentially with time. Furthermore, the room temperature-time constant associated with the photocurrent decay was 63 sec. for *o*-chloranil-violanthrene and 60 sec.

(10) H. Inokuchi, *Bull. Chem. Soc. Japan*, **24**, 222 (1951).

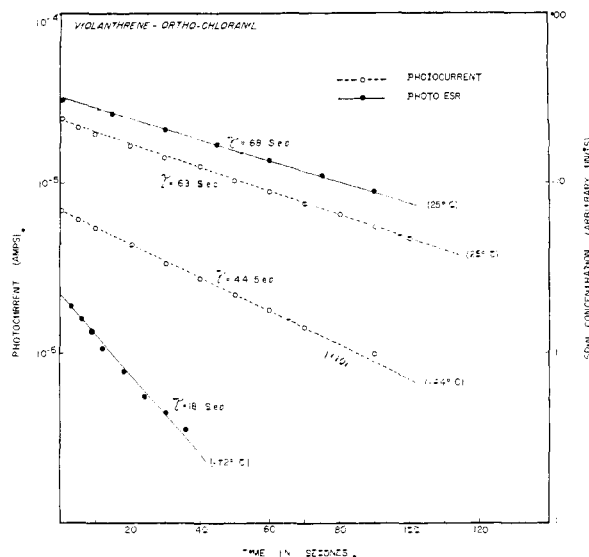


Fig. 4.—Semi-log plots of the time dependence of photoconductivity and light induced e.s.r. in violanthrene ($\sim 10^{-5}$ mole) treated with approximately 3×10^{-5} mole of *o*-chloranil.

for tetracyanoethylene-violanthrene. Accurate room temperature data were not obtainable with the iodine-violanthrene system. However, a time constant of 45 sec. was measured at -40° . Corresponding to this a 44 sec. time constant was observed for the *o*-chloranil-violanthrene system at -40° . When the temperature of an iodine-violanthrene cell was lowered to -60° , the photocurrent decay constant was decreased to 26 sec. In Fig. 4 the photocurrent decay data for an *o*-chloranil-violanthrene surface cell are shown. A summary of the photocurrent time constants for the three systems is presented in Table I.

TABLE I
COMPARISON OF PHOTOCURRENT AND PHOTO E.S.R. LOGARITHMIC DECAY CONSTANTS τ , ($N = N_0 e^{-t/\tau}$)

Violanthrene was the donor molecule used with one of the three electron acceptors *o*-chloranil (*o*-Q), iodine (I_2) or tetracyanoethylene (TCNE)

T, °C.	τ (seconds)			τ (seconds)		
	<i>o</i> -Q	I_2	TCNE	<i>o</i> -Q	I_2	TCNE
+25	63	..	60	68	69	67
-40	44	45
-60	..	26
-75	18	18	..

D. Intensity Dependence.—The steady state photocurrent at various light intensities was measured for a violanthrene surface cell doped with 6×10^{-5} mole of *o*-chloranil. An interference filter was used to restrict the exciting light to the range 4500–5500 Å. and neutral density filters were used to vary the light intensity. As can be seen from the data presented in Fig. 5, the photocurrent varied linearly with the light intensity.

Electron Spin Resonance.—Electron spin resonance measurements were carried out with a previously described spectrometer¹¹ in which samples could be illuminated while in the spectrometer cavity. The two types of samples used for these measurements were prepared as: (a) film samples: prepared by vacuum sublimation of violanthrene onto a glass support followed by treatment with the desired electron acceptor; (b) powder samples: prepared by grinding a mixture of desired composition of violanthrene and the electron acceptor.

A. Variation of the Unpaired Electron Spin Concentration with the Amount of Electron Acceptor Added.—Un-

(11) P. B. Sogo, N. G. Pon and M. Calvin, *Proc. Natl. Acad. Sci., U. S. A.*, **43**, 387 (1957).

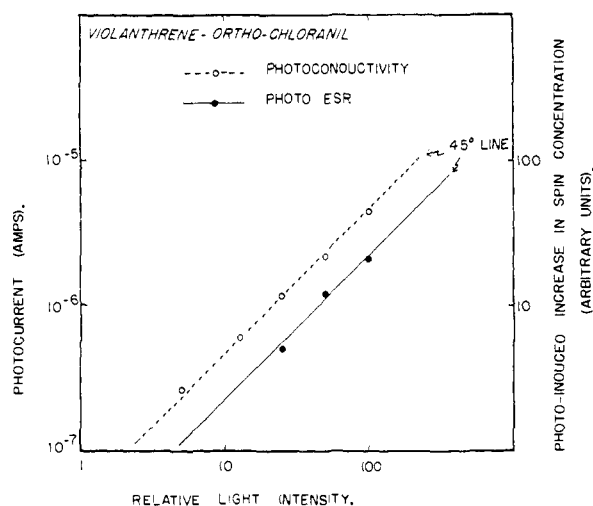


Fig. 5.—Intensity dependence of the steady-state photocurrent and photo-e.s.r. in violanthrene ($\sim 10^{-5}$ mole) treated with *o*-chloranil ($\sim 10^{-5}$ mole). In the photocurrent measurements, the maximum light intensity used was 3×10^{16} quanta/sec. of red light. The intensity of light impinging on the sample in the e.s.r. spectrometer was not measured.

treated violanthrene film samples were found to contain a measurable number of unpaired electron spins. The concentration of these spins increased with the length of time the sample was exposed to air. Freshly prepared samples contained less than 0.1% of the concentration of unpaired spins produced by doping with the weakest of the three electron acceptors, TCNE. The addition of any one of the three electron acceptors to a film of freshly sublimed violanthrene produced a large concentration of unpaired electron spins which increased when the amount of electron acceptor was increased. This effect is shown for the *o*-chloranil-violanthrene system in Fig. 3 along with the results of the conductivity measurements on this same system. Similar results were obtained with the iodine- and the tetracyanoethylene-violanthrene systems.

The absolute concentration of unpaired electrons in powdered samples of violanthrene with approximately 50% by weight electron acceptor was estimated from the ratio of the absorption intensity of the complex to that of a DPPH sample containing 3×10^{15} unpaired electrons. The ratio of no. unpaired spins/no. of violanthrene molecules was (see col. 5, Table II): violanthrene-iodine, 0.27; violanthrene-*o*-chloranil, 0.01; violanthrene-tetracyanoethylene, 0.001.

We see (Table II) that there is a correlation between number of unpaired spins produced by an electron acceptor when it is added to violanthrene and its effect on both the dark and photoconductivity of the violanthrene.

B. *g*-Values.—The Mn^{+2} ion in MgO exhibits an electron spin resonance (e.s.r.) absorption spectrum consisting of 6 main lines with a splitting of about 84 gauss between lines. The two-center lines were measured and found to have *g*-values of 2.031140 ± 0.0001 and 1.98150 ± 0.0001 , respectively.¹² Samples of MgO containing Mn^{+2} supported in polyethylene film were placed in contact with the organic samples during the electron spin resonance measurements. From the position of the center of e.s.r. absorption due to the organic donor-acceptor system relative to the positions of the two center lines of the Mn^{++} absorption, it was possible to calculate the *g*-value of the unpaired electrons in the organic systems.

Using this method a *g*-value of 2.0037 ± 0.0002 was obtained for a polycrystalline sample of DPPH, in good agreement with the results of others.¹³ The results of the *g*-value

(12) We are indebted to John Eastman for these results on the Mn^{++} ESR absorption and for the use of this standard sample prepared according to R. O. Lindblom, Thesis, University of California, Berkeley, 1959.

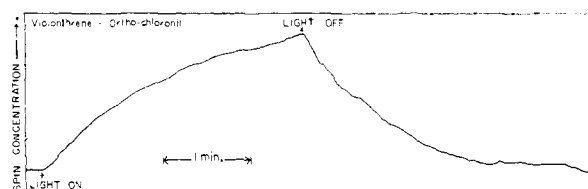


Fig. 6.—Effect of illumination with white light on the e.s.r. signal in *o*-chloranil-treated violanthrene. The curve represents unpaired spin concentration vs. time.

measurements on film and powder samples of the three violanthrene-acceptor systems are given in column 3 of Table II.

C. Line Width.—The line width at maximum slope of the e.s.r. absorption in the three violanthrene-acceptor systems was calculated by comparison with the splitting between lines in the Mn^{+2} spectrum. The results of measurement on both powder and film samples are shown in column 4 of Table II.

Photo-electron Spin Resonance.—When a film sample of violanthrene treated with any one of the three electron acceptors was illuminated in the electron spin resonance spectrometer cavity, a reversible change in the unpaired spin concentration could be observed. In the case of *o*-chloranil or tetracyanoethylene treated violanthrene, the effect of light was to increase the number of unpaired electron spins; however, in the case of iodine-violanthrene samples, light decreased the number of unpaired electron spins. The photo-induced changes in the unpaired spin concentration in the three systems amounted to several per cent. of the total unpaired spin concentration in the dark; these are collected in column 6 of Table II. This effect is shown in Fig. 6 for an *o*-chloranil-treated violanthrene film.

Following illumination, the spin concentration in each of the three cases returned to its steady-state dark value exponentially with time, with a room temperature decay constant of 67–69 sec. At -75° the time constant for photo spin resonance decay was 18 sec. for both the *o*-chloranil- and iodine-violanthrene systems. The photo-e.s.r. decay data for the three systems are summarized in columns 6 and 7 in Table II.

The light intensity dependence of the photo-induced unpaired spin concentration was measured for the *o*-chloranil-violanthrene film sample, and the results of these measurements are shown in Fig. 5. As one would expect for a process with unimolecular decay kinetics, the photo-induced unpaired spin concentration varied linearly with the light intensity.

Spectral Study.—The rather large concentration of unpaired electron spins found in the *o*-chloranil- and iodine-violanthrene systems suggested that the species giving rise to the unpaired electron spins in these systems might be detectable by a study of the solid state absorption spectrum in the visible region. In the experiments described below, films of violanthrene on glass slides were prepared by sublimation. These filmed slides were then placed in a Cary model 14 spectrophotometer and absorption spectra were measured. The absorption spectrum of a violanthrene film is shown in curve A of Fig. 7a. The slides then were removed and the exposed surface of the violanthrene film was then treated with one of three strong electron acceptors: BF_3 , *o*-chloranil or iodine. The BF_3 was applied by exposing the violanthrene slide to a BF_3 atmosphere. The *o*-chloranil and iodine were applied by sublimation. When solutions of the electron acceptors were sprayed onto the violanthrene film, the film was somewhat disrupted and much light was scattered. After treatment with one of these three compounds, the samples were returned to the Cary spectrophotometer and absorption spectra were remeasured. A sample holder was constructed for the spectrophotometer so that the samples always were held in the same position relative to the light beam before and after treatments. This eliminated errors which might be caused by the variation of film thickness at different points of the film. In Fig. 7a, curves B, C, D, give the difference between the absorption spectra

(13) D. J. E. Ingram, "Free Radicals Studied by Electron Spin Resonance," Butterworths Scientific Publications, London, 1958, p. 136.

TABLE II
ELECTRIC AND MAGNETIC PROPERTIES OF SOME DONOR-ACCEPTOR LAMELLAR SYSTEMS

1	2	3	4	5	6	7	8	9					10	11
								Current (amp.) passing through std. surface cell with 90 v. applied						
Donor molecule solid state ionization potential, (e.v.)	Acceptor molecule	g-Value \pm 0.002	Line width (gauss)	No. of unpaired electrons per donor molecule	Effect of illumination on the unpaired spin concn. (approx. % change)	Photo ESR decay constant, τ (sec.) ($N = N_0 e^{-t/\tau}$)	Photo-current decay constant, τ (sec.) ($N = N_0 e^{-t/\tau}$)	DC ^e	PC ^f	$\frac{DC^g}{DC^h}$	$\frac{PC^g}{PC^h}$	Mole of acceptor added	Dark current, cell ^k	Photo-current, cell ^k
Metal-free phthalocyanine (4.5)	<i>o</i> -Chloranil	2.0028	4.2 S ^b	0.002	D ^c (10%)	65	61	10 ⁻³	10 ⁻⁴	(5 × 10 ⁸)	× (5 × 10 ⁴)	2 × 10 ⁻⁵	20	10
	Iodine	2.0030	6.7 A ^b	.01	D (26%)	N.m.	N.m.	5 × 10 ⁻³	4 × 10 ⁻⁴	(× 2.5 × 10 ⁸)	(× 7 × 10 ⁴)	Subl. layer	N.m.	N.m.
	Tetracyanoethylene	2.0028	4.2 S	.001	D (36%)	(60)	N.m.	1.2 × 10 ⁻⁵	3 × 10 ⁻⁶	(× 10 ⁸)	(× 400)	10 ⁻⁴	N.m.	N.m.
Tetracene (4.8)	<i>o</i> -Chloranil	2.0029	4.2 S	.0003	I ^d (1%)	N.m.	N.m.	8 × 10 ⁻⁴	2 × 10 ⁻⁶	(× 4000)	(× 300)	6 × 10 ⁻⁵	15	4.2
	Iodine	2.0031	6.7 A	.08	D (26%)	N.m.	N.m.	7 × 10 ⁻⁸	7 × 10 ⁻⁸	(× 140)	(× 35)	+ 10 ⁻⁵	7	10
	Tetracyanoethylene	N.m. ^a	4.2 S	N.m.	N.m.	N.m.	N.m.	2.5 × 10 ⁻⁹	2 × 10 ⁻⁹	(× 3)	(× 3)	3 × 10 ⁻⁵	1.3	2
Pentacene (4.5)	<i>o</i> -Chloranil	2.0031	1.4 A	.001	N.m.	N.m.	N.m.	3 × 10 ⁻⁵	1.5 × 10 ⁻⁴	(× 10)	(× 10)	+ 10 ⁻⁵	2	2
	Iodine	2.0028	8.0 A	.12	N.m.	N.m.	N.m.						N.m.	N.m.
	Tetracyanoethylene	2.0034	2.5 A	.00005	N.m.	N.m.	N.m.						N.m.	N.m.
Violanthrene (4.6)	<i>o</i> -Chloranil	2.0030	4.0 S	.008	I (4%)	69	63						60	77
	Iodine	2.0028	7.2 S	.27	D (2%)	69		2 × 10 ⁻⁵	5 × 10 ⁻⁷	(× 104)	(× 4 × 10 ⁸)	6 × 10 ⁻⁵	580	200
	Tetracyanoethylene	2.0032	7.2 S	.0008	I (10%)	67	60						20	17
Decacycene (4.8)	<i>p</i> -Fluoranil	2.0032		.0003	N.m.									
	<i>o</i> -Chloranil	N.m.	3.4	.0005	N.m.	N.m.	N.m.						N.m.	N.m.
	Iodine	2.0029	6.7	.012	N.m.	N.m.	N.m.						N.m.	N.m.
Perylene (4.8)	<i>o</i> -Chloranil	N.m.	N.m.	.001	N.m.	N.m.	N.m.	6 × 10 ⁻⁷	6 × 10 ⁻⁷	(× 400)	(2 × 10 ⁸)	10 ⁻⁵	N.m.	N.m.
	Iodine	2.0033	5.8	.14	N.m.	N.m.	N.m.						N.m.	N.m.

^a N.m. = no measurement. ^b S = symmetric line shape, A = asymmetric line shape. ^c D = decrease. ^d I = increase. ^e DC = dark current. ^f PC = photocurrent. ^g Doped cell. ^h Undoped cell. ⁱ Treated with 10⁻⁵ mole of acceptor. ^k Treated with 2 × 10⁻⁶ mole of acceptor.

of the pure violanthrene films and the same films after treatment with BF_3 , *o*-chloranil or iodine. Quite clearly, addition of any of these three electron acceptors to a violanthrene film produces the same new absorption band with a maximum at approximately 7200 Å.; BF_3 produces the strongest absorption whereas *o*-chloranil and iodine result in smaller but nearly equivalent changes in the violanthrene absorption spectra.

From these spectra we conclude that the addition of any one of these three electron acceptors to violanthrene leads to the production of a new species which is the same in all three cases. Furthermore, since the electron acceptor is different in all three cases, the new absorption band cannot be attributed to the electron acceptor species or even to the formation of a charge transfer complex between violanthrene and the electron acceptor.¹⁴ But, rather, we must attribute the new absorption band to the formation of a new violanthrene species which is the same regardless of which electron acceptor is used to produce it.

The question now arises as to the identity of the new violanthrene species. The solid state ionization potential (I_{solid}) of violanthrene has been measured¹⁵ and found to be approximately 4.6 e.v. and the solid state electron affinity (E_{solid}) of *o*-chloranil was estimated to be at least 4.6 e.v. On the basis of these values, one would expect the addition of *o*-chloranil to violanthrene in the solid state to lead to the transfer of electrons from violanthrene molecules to *o*-chloranil molecules and the production of violanthrene positive ions and *o*-chloranil negative ions. It is therefore quite likely that the 7200 Å. absorption in the violanthrene-*o*-chloranil system is due to violanthrene positive ions; BF_3 is quite a strong electron acceptor and has even been used to produce the positive ion of various aromatic hydrocarbons in solution.^{16a,b} It is certainly reasonable that addition of BF_3 to violanthrene in the solid state will produce violanthrene positive ions. On the basis of these arguments, we conclude that the violanthrene positive ion is responsible for the new absorption produced by addition of iodine to violanthrene.

An examination of the absorption spectra of violanthrene dissolved in concentrated sulfuric acid provides additional evidence that the 7200 Å. solid state absorption in the violanthrene-electron acceptor systems is due to violanthrene positive ions. Weijland¹⁷ has carried out a thorough study of the sulfuric acid solution spectra of a number of aromatic hydrocarbons. In the case of anthracene, tetracene and perylene, it appears that the formation of a proton adduct runs parallel to the formation of the hydrocarbon positive ion. In the case of perylene and tetracene, however, the proton adduct spectrum disappears after a short time.

In our experiments, when the violanthrene was initially dissolved in concentrated sulfuric acid, the solution had absorption bands at 6400 and 6600 Å. The 6400 Å. absorption disappeared in about one-half hour, and at the same time the 6600 Å. absorption band became more intense (see Fig. 7b). After a period of 3 hours the 6600 Å. absorption also disappeared. Due to the similarity in the spectral behavior of the violanthrene in concentrated sulfuric acid with the spectral behavior of other aromatic hydrocarbons in concentrated sulfuric acid, we are tempted to ascribe the 6400 Å. absorption to a proton adduct of violanthrene and ascribe the 6600 Å. peak to the violanthrene positive ion in sulfuric acid solution.

Jacobs and Holt¹⁸ found that the absorption spectrum of crystalline ethyl chlorophyllide a is shifted by as much as 870 Å. to the red of the acetone solution spectrum of ethyl chlorophyllide a. If the 6600 Å. absorption is due to violanthrene positive ions in solution, then 7200 Å. is not unreasonable for the absorption band of violanthrene positive ions immersed in a solid matrix with a high fre-

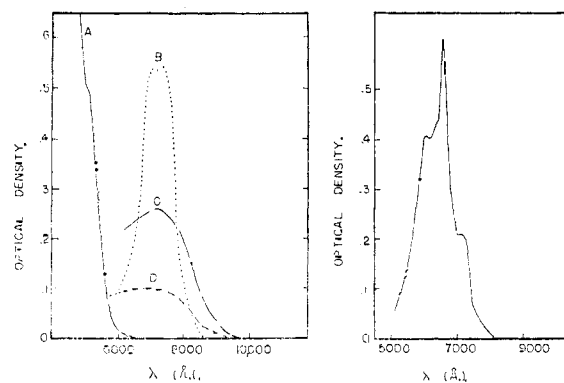


Fig. 7a (left).—A, solid state absorption spectrum of pure violanthrene; B, difference between the solid state absorption spectrum of violanthrene treated with BF_3 and that of pure violanthrene; C, difference between the solid state absorption spectrum of violanthrene treated with *o*-chloranil and that of pure violanthrene; D, difference between the solid state absorption spectrum of violanthrene treated with iodine and that of pure violanthrene.

Fig. 7b (right).—Absorption spectrum of violanthrene dissolved in concentrated sulfuric acid for one hour.

quency dielectric constant much larger than that of sulfuric acid. The sulfuric acid solution data do support the notion that the 7200 Å. absorption band in the solid violanthrene-electron acceptor systems is due to the violanthrene positive ions. We will find this information particularly useful when we try to interpret the solid state electrical and magnetic behavior of the violanthrene-electron acceptor systems.

III. Other Donor Matrices Treated with Electron Acceptors

The results of a detailed study of the electrical and magnetic properties of films of metal-free phthalocyanine treated with *o*-chloranil have already been presented elsewhere.^{2b} In this section we shall present the results of a study of some electrical and magnetic properties of the donors tetracene, pentacene, decacyclene and perylene (see Fig. 2) with the three electron acceptors, *o*-chloranil, iodine and tetracyanoethylene. Some results on the iodine- and tetracyanoethylene-phthalocyanine systems will also be presented in this section.

Conductivity Measurements. A. Dark Conductivity.—Surface cells of the donor molecules were constructed and treated with one of the three electron acceptors in exactly the same manner as described in the section on violanthrene. The variation of the dark conductivity with the amount of electron acceptor added was studied for the *o*-chloranil-, iodine- and tetracyanoethylene-tetracene systems and for the *o*-chloranil-pentacene system. In each case curves of dark current as a function of amount of electron acceptor added were qualitatively similar to those obtained for the violanthrene systems (see Fig. 3). As an arbitrary index of the effect of an electron acceptor on the dark conductivity of a particular donor, we have used the ratio of the dark current with 10^{-6} mole of acceptor added to the cell to the dark current after only 2×10^{-6} mole of acceptor had been added to the cell. (The question of the purity and conductivity of "undoped" material is unresolved.) These dark current ratios for the various systems studied are presented in column 10 of Table II. In column 9 of this table, we have given the current passing through surface cells of the various donors after they had been treated with the amount of electron acceptor indicated. Included in Table II (column 9) are the ratios of the dark currents obtained in the heavily treated donor surface cells compared to those of the "pure" donor cells.

(14) G. Briegleb and J. Czekała, *Angew. Chem.*, **72**, 401 (1960).

(15) D. R. Kearns and M. Calvin, *J. Chem. Phys.*, June, (1961).

(16) (a) W. Ij. Aalsberg, Thesis, Some Aspects of the Formation of Aromatic Hydrocarbon Positive Ions, Amsterdam, 1960; (b) W. Ij. Aalsberg, G. J. Hoijtink, E. L. Makor and W. P. Weijland, *J. Chem. Soc.*, 3055 (1959).

(17) W. P. Weijland, Thesis, Investigations on the Electronic Spectra of Alternant Aromatic Hydrocarbon Positive and Negative Ions, Amsterdam, 1960.

(18) E. E. Jacobs and A. S. Holt, *J. Chem. Phys.*, **20**, 1325 (1952).

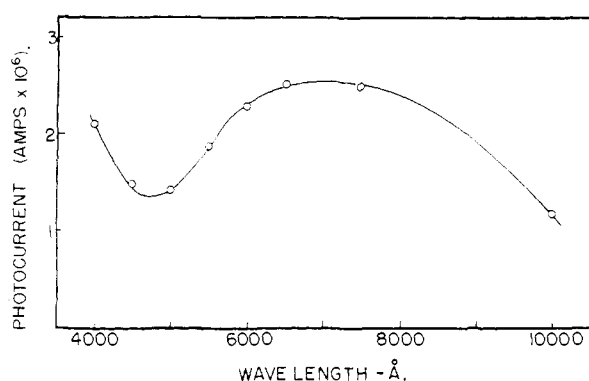


Fig. 8.—Spectral response of the steady-state photocurrent of *o*-chloranil with 2.5 mole % phthalocyanine.

B. Photoconductivity.—The variation of the photoconductivity with the amount of electron acceptor was studied for the *o*-chloranil-, iodine- and tetracyanoethylene-tetracene system as well as for the *o*-chloranil-pentacene system. Again, with each of these systems, the variation of the photocurrent with the amount of electron acceptor added was entirely similar to the results obtained with the three violanthrene systems (see Fig. 3). As an index of the effect of an electron acceptor on the photoconductivity, we have used the ratio of photocurrent obtained from a cell treated with 10^{-5} mole of acceptor per cell compared with the photocurrents obtained from a cell treated with 2×10^{-6} mole of electron acceptor. These data appear in column 11 of Table II. The photocurrent passing through a standard surface cell (see Fig. 1) treated with the amount of electron acceptor indicated, and with 90 volts applied to the cell, is given in column 9 of Table II.

Neither the temperature dependence of the photoconductivity nor the kinetics of the photocurrent decay were studied for the tetracene or pentacene systems.

Electron Spin Resonance. A. *g*-Value, Line Width and Unpaired Electron Spin Concentration.—Both film and powder samples of the donor-acceptor complexes were used for the electron spin resonance studies. The *g*-value and line width of the electron spin resonance and the concentration of unpaired electrons were measured for most of the possible donor-acceptor combinations using the three electron acceptors, *o*-chloranil, iodine and tetracyanoethylene with the five electron donors metal-free phthalocyanine, tetracene, pentacene, decacyclene and perylene.

The methods used to measure *g*-values and line widths are described in the violanthrene section, and the results of these measurements appear in columns 3 and 4, respectively, of Table II. Unpaired electron spin concentrations in powdered samples of the various donor-acceptor complexes containing approximately 50% by weight acceptor were estimated by comparison of the intensity of e.s.r. absorption of the complexes with that of a DPPH sample containing 3×10^{15} unpaired electrons. The results of these measurements appear in column 5 of Table II where the number of unpaired electrons per donor molecule present is given.

B. Photo-electron Spin Resonance.—The effect of light on the unpaired electron spin concentration in lamellar samples of metal-free phthalocyanine treated with *o*-chloranil has been studied previously.² Light was found to reversibly decrease the unpaired electron spin concentration; the return of the spin concentration to its steady state dark value after the light was turned off followed unimolecular kinetics. The room temperature-time constant associated with this decay was ~ 65 seconds. At -100° it was 36 seconds. The effect of light on the unpaired electron spin concentration in film samples of metal-free phthalocyanine treated with iodine or tetracyanoethylene has now been measured, and again it was found that light reversibly decreases the unpaired electron spin concentration in both cases. The photo-e.s.r. in the phthalocyanine-tetracyanoethylene system followed unimolecular kinetics with a room temperature time constant of ~ 60 sec.

The effect of light on the unpaired electron spin concentration in *o*-chloranil- and iodine-tetracene systems was also measured. The unpaired spin concentration was

increased by light when *o*-chloranil was the acceptor, but decreased when iodine was the acceptor.

The effect of light on the unpaired electron spin concentration in the various systems studied is indicated in column 6 of Table II along with the percentage change in the unpaired electron spin concentration as a result of illumination. The room temperature photo-e.s.r. time constants for a few of the systems are given in column 7 of Table II.

IV. *o*-Chloranil Matrix: The Effect of Added Electron Donor

In the following series of experiments, the roles of the donor and acceptor layers were reversed, in that surface cells of the electron acceptor, *o*-chloranil, were constructed and then treated with the electron donor, phthalocyanine. The addition of phthalocyanine was achieved by first covering the back surface of an *o*-chloranil surface cell with a fine layer of powdered phthalocyanine and then heating the cell to the *o*-chloranil melting point for a few seconds. This produced cells in which the phthalocyanine was located primarily on the back surface of the *o*-chloranil layer. In certain cases surface cells were constructed using powdered *o*-chloranil that contained an admixture of 2.5 mole % phthalocyanine. Surface cells were constructed from the powdered mixture by simply heating this material on a sample cell. Sandwich cells were constructed by compressing the mixture between two stainless steel pistons contained in a glass sleeve.

Dark Conductivity.—The specific conductivity of pure *o*-chloranil, as measured in a sandwich cell, was found to be $10^{-15} \Omega^{-1}\text{cm}^{-1}$. The temperature dependence of the conductivity obeyed the relation $\sigma = \sigma_0 e^{-\Delta\epsilon/kT}$ with $\Delta\epsilon = 1.5$ e.v. When 2.5 mole % of phthalocyanine was admixed with *o*-chloranil and formed into a sandwich cell as described above, the specific conductivity increased from 10^{-15} to $2 \times 10^{-13} \Omega^{-1}\text{cm}^{-1}$. When a surface cell of *o*-chloranil treated with phthalocyanine on the back surface was cooled from 25 to -50° , the specific conductivity decreased by a factor of 11. Assuming an exponential temperature dependence of $\sigma = \sigma_0 e^{-\Delta\epsilon/kT}$, a $\Delta\epsilon$ of 0.2 e.v. may be calculated.

Photoconductivity.—The photoconductivity of a surface cell of pure *o*-chloranil was found to be too small to obtain a spectral response curve. When a surface cell was illuminated (front face) with 10^{17} quanta/sec. of 6000-7000 Å. light, a photocurrent of 6.6×10^{-11} amp. was observed with 90 v. applied to the sample. Under these same conditions, the surface cell of *o*-chloranil doped with phthalocyanine produced a photocurrent of 3.3×10^{-9} amp., representing an increase of 5×10^8 in photoconductivity due to doping with phthalocyanine. When the temperature of this sample was lowered from 25 to -50° , the photocurrent also decreased by a factor of 11, indicating an activation energy for photoconduction of ~ 0.2 e.v.

The spectral response of the photoconductivity for the above surface cell is shown in Fig. 8 for back-face illumination. The phthalocyanine was fairly well localized to the back surface and the spectral response of the photocurrent resulting from illumination of this face corresponds to the phthalocyanine absorption spectrum.

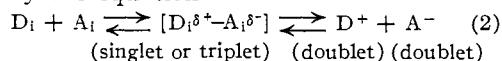
Electron Spin Resonance.—Pure *o*-chloranil had no observable unpaired electron spin concentration ($< 10^{13}$ spins/g.); however, phthalocyanine-doped *o*-chloranil had a high spin concentration. The shape of the spin resonance absorption was identical to that observed in the *o*-chloranil doped phthalocyanine samples.² Spin resonance measurements indicated a spin concentration of 3×10^{17} spins/g. in the sample used in the sandwich cell conductivity measurements described above. There were 2×10^{-4} mole of phthalocyanine per gram of this sample, and thus 3×10^{17} spins/g. corresponds to 1 unpaired spin per 400 phthalocyanine molecules.

V. Discussion and Conclusions

Dark Reactions.—Consideration of the solid state ionization potential of violanthrene (~ 4.6 e.v.) and the solid state electron affinity of *o*-chloranil (~ 4.6 e.v.) suggests that the formation of violanthrene monopositive ions and *o*-chloranil mononegative ions in the solid state is energetically possible. The absorption spectra of violanthrene films treated with *o*-chloranil tends to confirm this. Analysis of the absorption spectra of violanthrene films treated with iodine vapor indicates that electron transfer also occurs in the violanthrene-iodine system with the formation of some negative ion species of iodine and violanthrene monopositive ions. Consequently, the rather large electron spin resonance absorption observed in the *o*-chloranil- and iodine-violanthrene systems can be explained in terms of the formation of monopositive ion-radicals of violanthrene and mononegative ion-radicals of the electron acceptor. The fact that the tetracyanoethylene-violanthrene system also shows electron spin resonance absorption suggests that transfer of electrons from violanthrene to the tetracyanoethylene takes place to some extent. The exact nature of the species which are believed to give rise to the observed electron spin resonance will be discussed later.

In a similar fashion, the electron spin resonance absorption observed in the various other donor-acceptor systems studied is presumed to be due to the formation of monopositive donor ion-radicals and mononegative acceptor ion-radicals. The solid state electron affinity of *o*-chloranil is probably as large, or larger, than the solid state ionization potential of any of the six electron donors used¹⁴ (column 1, Table II). Therefore, in any one of these six donor-*o*-chloranil systems we should expect loss of electrons from the donor layer to the *o*-chloranil layer. Solid state electron affinities are not available for either iodine or tetracyanoethylene so we are not able to predict on this basis alone whether or not electron transfer from any one of the donors to these two electron acceptors would take place.

The electron transfer reaction which takes place when a donor and acceptor layer are placed in intimate contact with each other may be represented by the equation



where D_i and A_i represent neutral donor and acceptor molecules located at the donor-acceptor interface, $[D_i^{\delta+}-A_i^{\delta-}]$ represents a charge transfer complex and D^+ and A^- are singly charged donor and acceptor molecules, respectively. As indicated by this equation, partial separation of charge is accomplished by the formation of a charge transfer complex at the interface of the donor and acceptor layers. The degree of charge separation in the complex will determine the energy required to overcome completely the coulombic attraction between the positive and negative charge. The polarization energy associated with separated charge is greater than that for a dipole^{19,20} and for

(19) Bottcher, "Theory of Electrical Polarization." Elsevier Publishing Co., Amsterdam, 1952.

this reason the coulombic energy involved in completing the charge separation initiated in complex formation may be more than compensated for by a gain in polarization energy. The measured values of the solid state donor ionization potentials and the estimated *o*-chloranil electron affinity have already indicated that this should be the case in the *o*-chloranil-donor systems. Migration of charge in both layers may now take place by migration of electrons between identical molecular sites within a particular layer.

Once the positive and negative charges have moved several molecular diameters into the donor and acceptor layers, respectively, there will be only a small coulombic attraction between charges when the total amount of charge transferred is small, and the positive charges will be free to move throughout the donor layer as will the negative charges in the acceptor layer. It is postulated that the observed large increases in the dark conductivity of donor surface cells produced by the addition of electron acceptors to the back side of the cell are due to the production of mobile positive charges in the donor layer. In view of the geometry of the surface cell (see Fig. 1), it is reasonable that mobile charges in the region of the donor layer near the electrodes (conducting region) would make a larger contribution to the cell conductivity than would charges located some distance from the electrodes, *i.e.*, near the back face of the donor layer. Based upon results of studies of phthalocyanine surface cells of varying thickness,⁹ we presume this conducting region to be a layer extending about 10^{-5} cm. back from the electrode surface. It was shown with phthalocyanine, that if a surface cell is made thick enough, mobile carriers photo-produced at the back face make almost no contribution to the cell conductivity. The existence of such a conducting region in the other donor surface cells is indicated by the fact that front face illumination of a pure donor surface cell always produced larger photocurrents than did back face illumination.

As the number of electrons transferred from the donor layer to the acceptor layer increases, an electric field opposing the electron transfer develops. When the work required to move an electron against this electric field from the donor to the acceptor layer becomes equal to the energy gained from performing such an electron transfer in the absence of a field ($I_{\text{solid}} - E_{\text{solid}}$), then the net electron transfer will cease. A second consequence of the development of this electric field will be that positive or negative charges formed in the donor and acceptor layers, respectively, will tend to remain near the donor-acceptor interface.

On the basis of the proposed mechanism (eq. 2) there are several reasons why we expect the conductivity in the donor layer to be a sensitive function of the acceptor layer thickness. In the first place, the energy of negative charges in the acceptor layer will be lowered by increasing the number of polarizable molecules around them. If, as indicated in eq. 2, we assume that an equilibrium exists between charges located in the donor

(20) L. E. Lyons, *J. Chem. Soc.*, 5001 (1957).

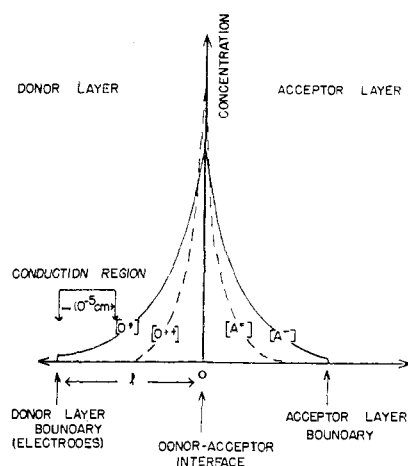


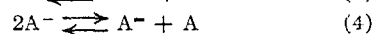
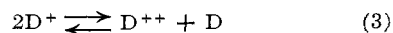
Fig. 9.—Hypothetical distribution of charges in a lamellar donor-acceptor system.

and acceptor layers, then the donor layer charge concentration will be a very sensitive function of acceptor layer thickness since the "equilibrium constant" for eq. 2 depends exponentially on the energy of the ions relative to the energy of the neutral molecules. This effect will probably be important for acceptor layers between 1 and ~ 10 molecules thick. The application of $\sim 10^{-6}$ mole of *o*-chloranil to a standard surface cell produces a layer about ~ 10 molecules thick.

A second effect of increasing acceptor layer thickness is to provide more sites for negative charge in the acceptor layer. If we assume an equilibrium exists between charges in the donor and acceptor layers, this will also lead to an increase in the concentration of charge in the donor layer. This second effect could be important over a large range of acceptor layer thickness. However, since charges in the two layers will tend to reside near the donor-acceptor interface, increase of the acceptor layer thickness beyond a certain point will have little effect in increasing the volume available to negative charges in the acceptor layer.

Thus, if we assume that an equilibrium exists between charges located in the donor and acceptor layers, we can understand qualitatively the variation of the donor layer conductivity with the acceptor layer thickness. This also explains why there are significant quantitative differences between different donor-acceptor systems since the equilibrium constant for electron transfer will be very sensitive to the ionization potential of the donor and the electron affinity of the acceptor.

As a result of the tendency of charge to accumulate near the donor-acceptor interface and as a consequence of the fact that the polarization energy of a double-charged ion (P_{++}) is four times that of a single-charged ion (P_+),¹⁹ the following reactions may be important



D^{++} is a dipositive donor molecule ion, A^{--} is a dinegative acceptor molecule ion, and both should be diamagnetic since they contain an even number of electrons. The polarization energy (P_+) of

a singly-charged ion in an aromatic crystal has been found to be approximately 1.9 e.v.¹⁵ Thus, reaction 3 will be important if the work required to remove an electron from a donor positive ion, does not exceed the first ionization potential of the donor by more than about 3.8 e.v. ($P_{++} - 2P_+ = 2P_+ = 3.8$ e.v.). The solid state ionization potential of violanthrene has been measured and found to be ~ 4.6 e.v., indicating a gaseous ionization potential of 6.5 e.v. If the gaseous appearance potential for violanthrene dipositive ions is less than ~ 17.0 e.v., then reaction 3 will be exergonic. For reaction 4 to take place spontaneously, the gaseous electron affinity of the neutral acceptor molecules must not exceed the electron affinity of the acceptor negative ion by more than ~ 3.8 e.v. In the case of *o*-chloranil, the gaseous electron affinity can be estimated from solid state electron affinity measurements to be $\sim +3.0$ e.v.¹⁵ Consequently, if *o*-chloranil negative ions have an electron affinity in the gas phase of ~ -1.0 e.v., then reaction 4 will also be exergonic.

We would expect the concentration of doubly charged ions in the region near the donor-acceptor interface to be higher not only because reactions 3 and 4 are favored in this region, but also because the electric field produced across the donor-acceptor layers would pull the doubly charged ions into this region more strongly than singly charged ions. A hypothetical distribution of charge is shown in Fig. 9. As indicated in this figure the conductivity electrodes are located at some distance l , from the donor-acceptor interface so that, according to the diagram, the large increases in the dark conductivity of a violanthrene surface cell which result from the addition of an electron acceptor are due to the production of a large concentration D^+ and/or D^{++} ions in the vicinity of the electrodes.

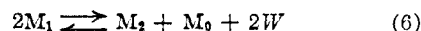
The above mechanism predicts that unpaired spin concentration and dark conductivity should increase concomitantly, but that a strict one to one relationship between spin concentration and number of carriers need not exist. The degree to which we can equate spin concentration and effective charge carriers will depend upon the thickness of the conducting region relative to the thickness of the sample and the degree to which reactions 3 and 4 take place. If the voltage applied to the sample electrodes were effective in drawing carriers from a large portion of the violanthrene layer and if reactions 3 and 4 were not important, then the number of carriers would be nearly equal to half of the total number of unpaired electron spins ($D^+ + A^-$). The presence of a high concentration of D^{++} or A^{--} ions in the sample will, of course, destroy such a simple relation between spin concentration and number of carriers.

Kaplan and Kittel²¹ have shown that the equilibrium constant for reactions such as 3 and 4 can be expressed as

$$K = [M_2][M_0]/[M_1]^2 = e^{2W/kT} \quad (5)$$

where M_2 is doubly ionized molecule, M_1 is a singly ionized molecule, M_0 a neutral molecule and $2W$ is the energy change involved in the reaction

(21) J. Kaplan and C. Kittel, *J. Chem. Phys.*, **21**, 1429 (1953).



The value of W depends not only upon the molecular species involved but also upon any electric fields in which they may find themselves. For low concentrations of ions, M_0 will be approximately $10^{21}/\text{cm.}^3$ and

$$[M_2]/[M_1]^2 = \sim 10^{-21} e^{2W/kT} \quad (7)$$

Thus, it is possible to have a major portion of the charge in the double ionized form if W is positive and/or if the concentration of charge is high. In the lamellar systems, ions will tend to concentrate in the region near the donor-acceptor interface and consequently while the concentration of ions in a donor or acceptor layer, based upon the total volume of the layer, appears to be low, the concentration of ions near the donor-acceptor interface may be very high. These notions will be useful in interpretation of the results of the photoconductivity and photo-electron spin resonance experiments.

The above analysis indicates that the observed electron spin resonance could be due primarily to D^+ ion radicals in the donor layer, or A^- ion radicals in the acceptor, or both. It was initially hoped that g -value and line width measurements would indicate the nature of the environment of the unpaired electrons. Values of g as high as 2.0077²² have been observed for some salts of chlorinated quinones. It was found, however, that the g -values for all the solid state donor-acceptor e.s.r. absorptions differed from 2.0030 by only ± 0.0002 , or approximately the experimental error (see column 4, Table II).

There exist the following possible explanations: i. Because of the mobility of the electrons which give rise to the e.s.r. absorption, the electrons may have very little orbital angular momentum. If this is the case, then all of the solids might exhibit very nearly the same g -value.¹² ii. The e.s.r. absorption is primarily due to the D^+ ion radicals which we would expect would all have approximately the same g -value. This, of course, requires that the principal form of the negative ions in the acceptor layer be the diamagnetic A^- ions. iii. The principal ion species in the donor layer is D^{++} and the e.s.r. absorption is primarily due to A^- ion radicals. Again, we would require the absence of an orbital contribution in the acceptor layer.

Consideration of the line width of the e.s.r. absorption in the various donor-acceptor complexes is also of little value in allowing us to discover the nature of the environment of the unpaired electrons. The e.s.r. line width for the various donor-iodine complexes is always 6-8 gauss, while the line width is generally, though not always, narrower for the other donor-acceptor complexes. This suggests that in the various donor-iodine complexes, at least some of the e.s.r. absorption is from a species associated with the iodine layer. With regard to the other donor-acceptor systems, it is certainly not clear from the

(22) H. Kainer, D. Bijl and A. C. Rose-Innes, *Nature*, **178**, 1462 (1956). This value appears to be low. A corresponding value of 2.0094 for *o*-bromanil has been found by J. Eastman (University of California, Thesis, 1961).

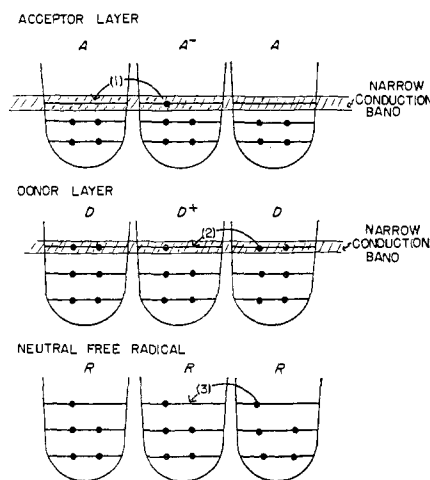


Fig. 10.—Charge migration in a molecular lattice. Schematic representation of donor and acceptor molecules and ions imbedded in a donor layer or an acceptor layer, respectively. From this diagram, it is clear that process (1), the transfer of an electron from an acceptor negative ion to a neutral neighbor, produces a state of the system which is energetically identical with the initial state. Similarly, there is no net change in energy as a result of process (2) which rearranges charge in the donor layer. In the case of a neutral free radical, however, the electron transfer process (3) does not result in a state energetically equivalent to the initial state. Since processes (1) and (2) simply change the location of negative and positive charges, respectively, with no net change in energy, we can consider the orbitals involved in the electronic rearrangements as forming conduction bands. If, however, the lattice were made up entirely of A^- radical ions (no A 's) irrespective of the cations, or entirely of D^+ radical ions (no D 's) irrespective of the anions, there would be no identical vacant orbitals into which the charge carriers could move and hence no conduction bands (however narrow). This last situation would correspond to the completely filled free radical system as in process (3) above.

line width data that the species giving rise to the e.s.r. absorption is A^- , D^+ , or both A^- and D^+ .

Before entering into a discussion of the photo-properties of lamellar donor-acceptor systems, the effect on the dark conductivity of introducing negative charge into an acceptor layer should be considered. We expect a positive charge introduced into the donor layer to be mobile and there is no reason why negative charges introduced into the acceptor layer should not also be mobile (Fig. 10). In the only experiment in which this effect was studied, the dark conductivity of *o*-chloranil was increased from $10^{-15} \Omega^{-1}\text{cm.}^{-1}$ to $2 \times 10^{-7} \Omega^{-1}\text{cm.}^{-1}$ by the addition of the 2.5 mole % of the electron donor, phthalocyanine, in conformation of our expectations that the negative charges in the acceptor layer are mobile. Unfortunately, no other acceptor-layer conductivity measurements have as yet been carried out.

Photoreactions.—The effect of light on the lamellar donor-acceptor systems can be best understood by considering the results of the photo-conductivity and photo-electron spin resonance together. It was found that the addition of any

one of the three electron acceptors *o*-chloranil, iodine or tetracyanoethylene to any one of the donor surface cells always increased the photoconductivity of the cell. The fact that the addition of an electron acceptor to a donor surface cell always enhances the photoconductivity produced by back face illumination more than it enhances the photoconductivity produced by front face (electrode) illumination, allows us to conclude that light is most effective in producing charge carriers (in the lamellar systems) when excited molecules are produced at or near the donor-acceptor interface. Following illumination, the photocurrent decay in these lamellar systems was found to obey unimolecular kinetics with a room temperature time constant of approximately 60 seconds. At lower temperatures, the time constant was shorter.

When a lamellar donor-acceptor complex was illuminated in the e.s.r. spectrometer, a reversible change in the e.s.r. absorption was observed. In certain cases, light caused an *increase* in e.s.r. absorption, but in others the e.s.r. absorption was *decreased*. An important fact regarding the photoelectron spin resonance absorption is that following illumination the return of the unpaired electron spin concentration to an equilibrium dark value always followed unimolecular kinetics with a room temperature time constant of approximately 65-70 seconds (see column 7 of Table II). Just as was observed for the photo-current decay time constant, the photo-e.s.r. decay time constant became shorter at lower temperatures (see Tables I and II). In the violanthrene-*o*-chloranil system both the photocurrent and the photo-e.s.r. varied linearly with the light intensity as anticipated for processes with exponential decays. These data clearly indicate that the photo-process which gives rise to the increase in the conductivity of the donor layer is the same process which produces a change, be it an increase or decrease, in the total unpaired electron spin concentration in the lamellar donor-acceptor complex.

From the results of a detailed investigation of the properties of metal-free phthalocyanine surface cells treated with *o*-chloranil, it was concluded that the effect of light on this donor-acceptor system was to increase reversibly the total positive charge in the phthalocyanine layer and to increase the total negative charge in the *o*-chloranil layer.^{2b} Because of the essential similarity in behavior of the phthalocyanine-*o*-chloranil system to all of the other donor-acceptor systems, it is postulated that illumination of the region near the donor-acceptor interface results in a photo-induced transfer of electrons from the donor layer to the acceptor layer and not the reverse. It is hard to envisage a situation where the return of electrons to the donor layer could result in an increase in the conductivity rather than a decrease at these high hole concentrations.²³ If light increases the concentration of positive charge in the donor layer and negative charge in the acceptor layer, it is clear this will result in an increased number of charge

carriers in the conduction region of the donor layer, but it is not immediately clear what the effect of light will be on the concentration of unpaired electrons.

The effect on the unpaired spin concentration in the acceptor layer (the same analysis applies to the donor layer) of increasing the charge concentration in that layer can be determined by use of eq. 5. If the charge concentration in the region near the donor-acceptor interface is

$$N = [A^-] + 2[A^{\cdot-}] \quad (8)$$

and the concentration of molecules is

$$M = [A^0] + [A^-] + [A^{\cdot-}] \quad (9)$$

where $[A^0]$ is the concentration of neutral molecules. Then we can obtain from 5 the following expression for A^-

$$A^- = \sqrt{\frac{2N \left(M - \frac{N}{2} \right)}{4K - 1}} \div \left(\frac{M}{4K - 1} \right)^2 - \frac{M}{4K - 1} \quad (10)$$

If we differentiate this expression with respect to N , we obtain

$$\frac{d(A^-)}{d(N)} = \frac{2(M - N)}{\sqrt{2(4K - 1) N \left(M - \frac{N}{2} \right)} \div M} \quad (11)$$

A similar expression can be obtained for $d(D^+)/dN$.

From eq. 11 we can see that if the charge concentration is increased the spin concentration will be *increased* if $(M - N)$ is positive and will be *decreased* if $(M - N)$ is negative.

The average concentration of unpaired electrons was found to range from $\sim 3 \times 10^{17}$ spins/cm.³ to 3×10^{20} spins/cm.³ in the system in which photo-effects were studied. Actually, this represents a rather high concentration of charge at the donor-acceptor interface since charges tend to be concentrated more in this region. Since the distribution of charge as well as the total number of molecules in a donor and acceptor layer need not be the same, and most likely will not be, it is possible for $(M - N)$ to be positive in one layer and negative in the other. In this case, the effect of light on the total unpaired spin concentration may be either positive or negative depending upon whether the spin change in the donor or acceptor layer is larger.

When phthalocyanine, tetracene or violanthrene are the donors and iodine is the acceptor, light always produces a *decrease* in the unpaired spin concentration. Average spin concentrations range from 0.01 to 0.3 unpaired spins per donor molecule so that in these three systems $(M - N)$ is quite reasonably negative in both the donor and acceptor layers near the interface.

When *o*-chloranil is the acceptor, and if phthalocyanine is the donor, light *decreases* the unpaired spin concentration whereas light *increases* the unpaired spin concentration if either tetracene or violanthrene are the donors. This is a bit surprising since the total spin concentration in the phthalocyanine-*o*-chloranil system appears to be lower than the spin concentration in the violanthrene-*o*-chloranil system. This suggests that charges in the phthalocyanine and *o*-chloranil layers tend

(23) One possibility for this exists; namely, that in which every donor molecule is in the D^+ condition, thus leaving no identical vacant orbitals into which the charge carriers can move; see the caption to Fig. 10.

to remain more concentrated near the donor-acceptor interface than do charges in violanthrene. Therefore, $(M - N)$ is negative for both layers of the phthalocyanine-*o*-chloranil system, while $(M - N)$ is positive in the violanthrene layer when the average spin concentration is large enough to make $(M - N)$ negative in the *o*-chloranil layer. Thus, it appears that the photo-induced increase in spin concentration in the violanthrene layer is slightly larger than the photo-decrease in the *o*-chloranil layer. The spin concentration in the tetracene-*o*-chloranil layer is lower than in either the phthalocyanine- or violanthrene-*o*-chloranil systems. In this case $(M - N)$ is probably positive for both the donor and acceptor layers; hence a photo-induced *increase* in unpaired spin concentration results.

Light *decreases* the unpaired spin concentration in the phthalocyanine-tetracyanoethylene system suggesting that $(M - N)$ is negative for both layers. Light *increases* the unpaired electron spin concentration in the violanthrene-tetracyanoethylene system when the average spin concentration is approximately the same as in the phthalocyanine-tetracyanoethylene system. Since $(M - N)$ is probably positive for the violanthrene, when the spin concentration was ten times larger (*o*-chloranil as the acceptor) it must certainly be positive when tetracyanoethylene is the acceptor. Although $(M - N)$ may or may not be negative in the tetracyanoethylene layer, the photo-induced increase in the spin concentrations in the violanthrene layer is much larger than any decrease in the tetracyanoethylene layer. Table III gives a summary of the probable sign of $(M - N)$ at the donor-acceptor interface layer for the systems discussed above.

It appears from the photo-e.s.r. measurements, that in any one of the three acceptor layers *o*-chloranil, iodine or tetracyanoethylene the charge concentration is always quite high ($(M - N) < 0$) near the donor-acceptor interface even for rather low spin concentrations. In other words, most of the charges in these acceptor layers are in regions of high charge concentration where A^{\bullet} would tend to be favored. If this is in fact the situation, it would explain why the *g*-values of all of the various donor-acceptor systems are approximately 2.0030 ± 0.0002 , since they would arise from unpaired electrons primarily in the donor layer.

We have postulated that light increases the concentrations of charge in both the donor and ac-

TABLE III
PREDICTED PROBABLE VALUES FOR THE SIGN OF $(M - N)$
IN THE INTERFACE LAYERS OF THE DONOR-ACCEPTOR
LAMALLAE

Donors	Acceptors	No. of unpaired electrons per donor molecule	Effect of light on the unpaired spin concn.	Probable sign of $(M - N)$ in the interface region	
				Donor layer	Acceptor layer
Phthalocyanine	<i>o</i> -Chloranil	0.002	D	-	-
	Iodine	.01	D	-	-
	Tetracyanoethylene	.001	D	-	-
Tetracene	<i>o</i> -Chloranil	.0003	1	+	±
	Iodine	.10	D	-	-
	Tetracyanoethylene				
Violanthrene	<i>o</i> -Chloranil	.008	1	+	-
	Iodine	.30	D	-	-
	Tetracyanoethylene	.0005	I	+	±

ceptor layer near the interfacial region and hence increases the concentration gradient which causes charge to diffuse away from the interfacial region. When the light is removed, the concentration gradient decreases due to recombination of charges at the interface, and carries in one layer drift back toward the interfacial region under the influence of the field of charges of opposite sign in the other layer. If the migration of carriers back toward the donor-acceptor interface, due to the reduction of the photo-induced concentration gradient, is the rate-limiting step in the recombination of charges, then the decay of both the photo-current and the photo-e.s.r. would have the same time constants. There is evidence^{9,24,25} which indicates that carrier mobilities in the organic solids *increase* when temperature is decreased, and this may explain why photoconductivity and photo-e.s.r. decay rates become faster at low temperatures. The fact that photoconduction is enhanced when the temperature is increased could be due to either (i) a shift in charge distribution within each of the layers with a change in temperature or (ii) electrode contact effects.

A more thorough investigation of these aspects will be required to resolve the problem.

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