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Effect of State of Order on the Photoconductivity of Auramine†

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The diagram of energy levels associated with generation, transport, and trapping of charge carriers in the dye auramine is investigated for four states of order of the solid ranging from loosely packed sublimed films to good single crystals. Within small classical corrections, all states yielded identical diagrams, consistent with the use of the localized model for photoconductivity in this material.

INTRODUCTION

Although organic solids are bound by van der Waals forces and charge transport in them is a weak phenomenon, a considerable amount of work has been done on their photoconductivity because of the significance of charge carrier generation for problems of energy conversion. The earlier work on anthracene and similar materials was disappointing because it became apparent that many of the phenomena arose from electrode effects. This is not true of the photoconductivity of dyes in general. Cho, Nelson, and Brown[1] investigated some members of a class of dyes in which a long relaxation time of the conductive excited state permitted a considerable population of spins to be built up in the solid by excitation of the lowest singlet transition. In these materials the kinetics of the rise and decay of photoconductivity could be reproduced from studies of the rise and decay of spin

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density. Identification of the unpaired spins with (trapped) conduction electrons led to reasonable mobilities, and it was evident that the interpretation of the conductivity in terms of density of carriers in the solid was justified. Since no electrodes or dc fields were present in the epr experiments, the phenomena must arise from intrinsic properties of the material itself.

It is a matter of some interest to know to what extent the properties of the solid depend on the existence of long range order. To our knowledge, no comparative study of the energy levels associated with photoconductivity in van der Waals solids has been carried out which includes a series of states of aggregation ranging from completely disordered films to good single crystals. Such a study offers an opportunity to determine whether the generation of charge carriers is basically intermolecular or localized in character or whether elements of the band model can be applied.

The dye used in this study was auramine hydrochloride (*p,p'*bis-dimethylaminophenylketimine hydrochloride) which is qualitatively identical in its behavior with the dye rhodamine-B investigated by Cho, *et al.* It has also the advantage of simpler and more symmetrical structure, leading to better stability, greater ease of purification, and the availability of single crystals of good quality.

ENERGY LEVELS AND TRANSITION ENERGIES

Optical and thermal measurements on dyes of this type lead to an energy-level structure of the sort shown in Figure 1. In the single electron formalism used, the energy levels are binding energies referred to the coventional zero

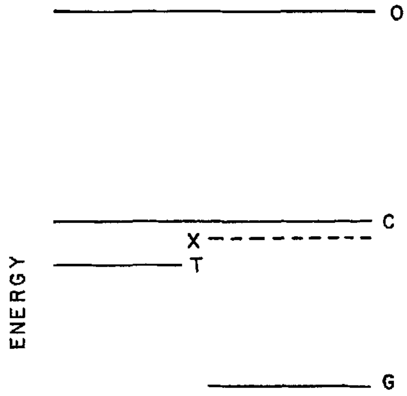

FIGURE 1 Diagram showing single-electron binding energies in solid auramine hydrochloride: *G*, ground state; *X*, excited state; *T*, characteristic trap; *C*, conductive state; and 0, conventional zero.

of an electron at rest at a distance. G is the energy with which the highest-lying electron in the ground state is bound; X, the energy of the optical electron of the excited state; C, the energy of a conduction electron; and T, the energy of an electron in the sort of trap which is found in all states of aggregation of auramine, and is characteristic of the material. Although the energies are defined empirically, they lead to self-consistent, over-determined energy level schemes for a variety of dyes.

The transition $G \rightarrow 0$ is measured by the external photoelectric effect; it is the surface ionization energy of the solid. The yield of electrons/incident photon increases exponentially in the threshold region and the threshold is defined empirically as the point at which the yield is 10^{-4} of the largest attainable yield at shorter wavelengths. $T \rightarrow 0$ is measured and defined in the same way. Nelson has shown that the ionization energy of a dye adsorbed as a monolayer on a dielectric substrate is given by

$$E_s = E_0 - C[(\kappa - 1)/(\kappa + 1)]$$

where E_0 is the vacuum ionization energy of the two-dimensional aggregate, and κ is the optical dielectric constant of the substrate.[2] We have measured the ionization energy of auramine adsorbed on glass and on cadmium sulfide to determine values of C and E_0. The measured surface ionization energy of the solid leads to a value of κ which is the effective dielectric constant of the bulk dye as it affects the surface ionization energy. The value of κ so found is indicative of the degree of packing of the substrate and of the sort of interaction between surface molecules and those lying immediately beneath them.

The dark conductivity of the dye is proportional to a Boltzmann factor $\exp(-E_d/kT)$. Neither E_d nor $2E_d$ can be identified with any transition on the energy level diagram.[3]

A photoconductive threshold energy is measured by allowing a cell to come to a steady state in the flux from a monochromator at a series of wavelengths. The threshold is defined arbitrarily as the point at which the response in arbitrary units per incident photon is 10^{-3} times that at the peak. This energy is associated with the transition $G \rightarrow X$.

The photoconductivity of auramine shows an initial slope of rise at the onset of irradiation which is proportional to the irradiance, and a steady state photoconductivity varying as $I^{\frac{1}{2}}$. The photoconductivity at constant irradiance increases with temperature as $\sigma = \sigma_0 \exp(-E_{th}/kT)$. E_{th} is interpreted as the dissociation energy of an exciton, and $E_{th}/2$ is assigned to the transition $X \rightarrow C$, the factor of 1/2 arising from the second-order kinetics.[5]

Like other dyes of the same type, many minutes are required for the photoconductivity of auramine to reach a steady state in light. After irradiation is discontinued, two stages in the decay process can be identified, a period of about five seconds in which 10–20 % of the conductance is lost, followed by a slow decay which obeys accurately the law $d\sigma/dt = -\alpha\sigma^2$ mimicking the decay of an intrinsic photoconductor.[4] The microscopic rate equation, $dn/dt = -an^2$ is related to the macroscopic by $\sigma = \mu ne$; if μ is constant so that σ is a valid measure of n, the macroscopic rate equation will be second order. There are two simple cases in which this can be true; if these are no traps, or if the traps are mono-energetic and the carriers are in equilibrium between traps and conductive state so that their mean mobility is constant. In dyes of this type there is a body of evidence tending to show that the traps are nearly monoenergetic,[1] and that trap-untrap processes limit the rate of decay.[4] The rate of decay is thus temperature-dependent and varies as the Boltzmann factor $\exp(-E_{tr}/kT)$. We assign E_{tr} to the transition $T \rightarrow C$.

EXPERIMENTAL

Technical grade auramine hydrochloride of about 70% purity was recrystallized three times from absolute methanol, then subjected to an acid-base fractionation procedure based on that of Lewis, *et al.*[6] The product was converted to the free base, sealed in a glass tube, and further purified by zone melting. The tube was passed vertically through the heater at about 1 cm/hr and the melted zone was less than 5% of the length of the charge. Twenty to thirty passes were made. The central part of the charge was reconverted to the chloride, crystallized from absolute methanol, and stored in a desiccator. The crystals weather in the presence of water vapor and crystals exposed to moist air more than briefly cannot be used under vacuum because of a tendency to shatter.

Table I gives values of some activation energies and other quantities as they changed during progressive stages of purification. The end of the zone melt carrying impurities with distribution coefficients less than unity was

TABLE I

Properties of films of auramine during purification

	Degree of Purification			Zone Refined	
	Crude	Recrystallized	Chemically Fractionated	Middle	End
Steady-state photocurrent/ dark current	1	2.2	100	220	3
Activation energy for dark conduction, eV		0.70	0.80	0.80	0.62
Activation energy for photoconduction, eV		0.59	0.26	0.26	0.28
Activation energy for 2nd order decay, eV			0.48	0.50	

comparable to the recrystallized starting material. It should be noted that the activation energies reach their final value before the purification is complete.

Four states of aggregation of the dye were examined:

1) Sublimed films were produced by rapid evaporation of the material onto a cold fused quartz surface carrying chemically deposited platinum electrodes. Such electrodes are ohmic to auramine and most cationic dyes, but do not behave well with non-ionic dyes. The evaporation was carried out at a pressure $< 10^{-5}$ torr. Tests showed no degradation of the dye in the process; the films were dark between crossed polarizers.

2) Auramine and many other common dyes can be formed into the so-called "continuous" films when a concentrated solution spread over a surface is evaporated rapidly.[7] Thick specimens show vitreous fracture. The films are dark between crossed polarizers, but X-ray diffraction work suggests the presence of one-dimensional local order.[8]

3) Polycrystalline films of auramine are best formed by treating a heavy sublimed film with saturated methanol vapor in the absence of air. These films are bright between crossed polarizers, and the crystals are microscopic in size.

4) Good single crystals of auramine are readily made by slow evaporation of solvent. They are regular hexagonal plates of thickness ~0.1 mm and up to 2 cm across. Small ones can be cemented to a flat surface with a little saturated auramine solution in absolute methanol.

DISCUSSION

The results of the optical and thermal transition energy measurements are shown in Table II. The activation energy for dark conduction is the same for all states of aggregation, as is the activation energy for photoconductivity. E_{tr} cannot readily be measured for sublimed films, but has the same value for the continuous films as it has for the single crystal. Small differences appear in the optical threshold energies which can be ascribed to classical dielectric effects. The low effective κ for sublimed films indicates that they are indeed loosely packed; the values of κ near 2.7 for the other states are unremarkable. Here, as in previously reported cases, the data are consistent with the idea that the surface dye molecule sees the bulk of the solid as a classical dielectric.[2]

It may be noted that there are two independent combinations of transition energies which can be used to compute the binding energy of the conduction electron: $G - X - E_{th}/2 = 2.85 \pm 0.05$ eV for the crystal, and $T - E_{tr} = 2.78 \pm 0.04$ eV. Direct measurement of C by the electron beam retardation methods gives 2.8 eV. This satisfactory agreement lends plausibility to the assignment of activation energies to transitions.

Since the identification of $G \rightarrow X$ is unmistakeable, the self-consistency of the energy level diagram makes it highly probable that the generation of charge carriers is an intrinsic property of solid auramine. The nature of the traps and the trapping process is a more difficult equation. Acid-base fractionation and zone melting rely on different characteristics of the dye and are thus independent, but there was no evidence of a diminution of traps associated with either. Since the traps are in any case generated during irradiation,[4,9] and thus cannot be due to impurities in any simple sense, our viewpoint toward them is that of Nelson,[3] who regards the filled trap as a molecule of the normal constituent plus an electron, in the configuration of the free radical to which it is equivalent.

TABLE II

Optimal and thermal transition energies in auramine

	Sublimed	Continuous	Polycrystalline	Crystal
Dark conduction	0.78	0.79	0.79	0.80
Thermal energy for photoconductivity	0.26	0.26	0.26	0.26
Thermal energy for 2nd order decay		0.47		0.48
Thermal energy for mobility		0.50		0.50
Optical threshold, photoconductivity	2.35	2.30	2.30	2.28
One-photon ionization	5.41	5.28	5.28	5.26
Associated dielectric constant	1.8	2.7	2.7	2.9
Ionization energy for trapped electron	3.14	3.22	3.24	3.26
Associated dielectric constant	2.0	2.6	2.8	2.9

These results are consistent with the localized model in which the basic processes of charge carrier generation and transport are essentially intermolecular, so that long range order is not required for their existence. This result is significant in connection with the mechanism of such sensitized processes as photosynthesis and the primary photographic process, in which the sensitizing molecules are in aggregates having at most local order.

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