
ATTI ACCADEMIA NAZIONALE DEI LINCEI
CLASSE SCIENZE FISICHE MATEMATICHE NATURALI
RENDICONTI

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**Electrical Conductivity of Biological and Organic
Compounds. Part VII. Dark Conductivity of
Aromatic Oxygen, Sulphur and Selenium Derivatives**

*Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche,
Matematiche e Naturali. Rendiconti, Serie 8, Vol. 55 (1973), n.3-4, p.
260-270.*

Accademia Nazionale dei Lincei

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Chimica. — *Electrical Conductivity of Biological and Organic Compounds. Part VII. Dark Conductivity of Aromatic Oxygen, Sulphur and Selenium Derivatives.* Nota (*) di PIER GIORGIO FUOCHI (**), GABRIELE GIRO (**), PIER GIULIO DI MARCO (**) e ALBERTO BRECCIA (***), presentata dal Socio G. SEMERANO.

RIASSUNTO. — È stato studiato il processo di semiconducibilità in alcuni selenoderivati organici, in tioxantene e xantene, sotto forma di polveri compresse. I valori di $\Delta\epsilon$ e di σ mostrano una buona riproducibilità. Inoltre i valori di $\Delta\epsilon$ sono inferiori alle energie del primo singoletto eccitato. I risultati sono spiegati in base al meccanismo di iniezione di portatori di carica in presenza di stati superficiali variabili con la temperatura.

INTRODUCTION

The present Note reports on the semiconductive properties of selenoxanthone, selenoxanthene, thioxanthene, xanthene and other organic selenium derivatives with a view to determining the possible effects of different heteroatoms and functional groups on electrical conductivity in a simple series of organic molecules. The problem of conduction in these poorly conductive aromatic molecules [1] (fig. 1) is re-examined in the light of the most recent results on charge carrier injection mechanism.

All the substances examined show a temperature dependence of conductivity according to the relationship $\sigma = \sigma_0 \exp(-\Delta\epsilon/2 kT)$ and the observed values of σ , σ_0 and $\Delta\epsilon$ vary widely from substance to substance; the data obtained were reasonably reproducible.

EXPERIMENTAL

Materials.

Fluka research grade xanthene and thioxanthene were purified by chromatography and then recrystallized from *n*-pentane.

The other compounds were prepared at the Department of Industrial Chemistry of the University of Bologna and were recrystallized several times from ethanol and ligroin.

The purity of all compounds was checked by T. L. chromatographic analysis, U. V. spectroscopy and melting point determination [2].

(*) Pervenuta all'Accademia il 22 settembre 1973.

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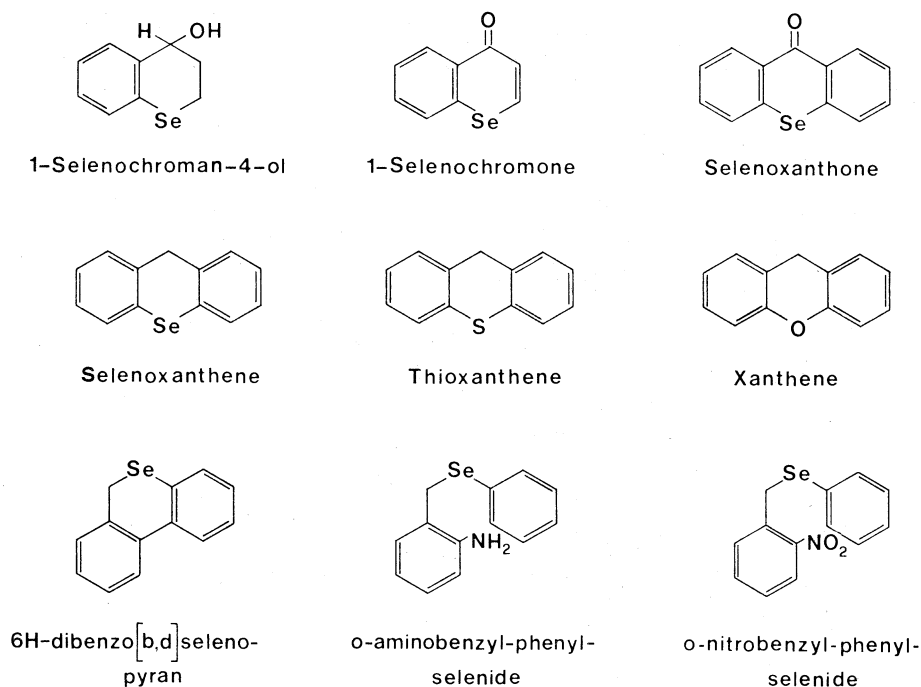


Fig. 1. — Investigated substances.

Preparation of Specimens.

Since attempts to grow single crystals of suitable sizes were unsuccessful for most of the substances, we used the standard method of measuring the electrical properties of the solids in the form of compressed powders [3a].

After crushing in an agate mortar the substances were dried, where possible, in a vacuum dessicator at 10^{-4} torr for 15 hours then placed between the electrodes of the measuring device. A pressure of 95 kg/cm² was then applied on the specimen with a calibrated spring exerting the desired pressure onto the electrodes and maintained throughout the measurements, yielding discs of 0.70 cm in diameter and 0.05–0.15 cm thick.

The pressure chosen is the pressure required to eliminate contact resistances and get homogeneous discs [3, 4].

Equipment and Technique.(a) *Conductance cell.*

The conductance cell based on that described earlier [5] was enclosed in a metallic container connected to a vacuum system.

The measurements were carried out in a nitrogen atmosphere after several evacuation-nitrogen purge cycles. Nitrogen was introduced through gas washers filled with Drierite.

Two heating resistances were used to raise the temperature which was measured with a chromel-allumel calibrated thermocouple close to the electrodes.

(b) *Measurement of current.*

The very low conductance levels of less than $10^{-11} \text{ ohm}^{-1} \text{ cm}^{-1}$ of the solids will cause the time constant of any measuring circuit to be very high. Therefore the use of a.c. methods had to be ruled out. The d.c. method [6] was employed and current measurements were carried out by means of a Keithley Model 417 High-Speed Picoammeter. All the electrical connections were made by double shielded teflon cables, heaters were non-inductively wound and thus we were able to reduce the random noise down to 10^{-13} amps.

The applied voltage of 200 V was taken from series connected high-tension dry batteries. The temperature range was from 30 to 100°C, depending upon the melting point of the specimen.

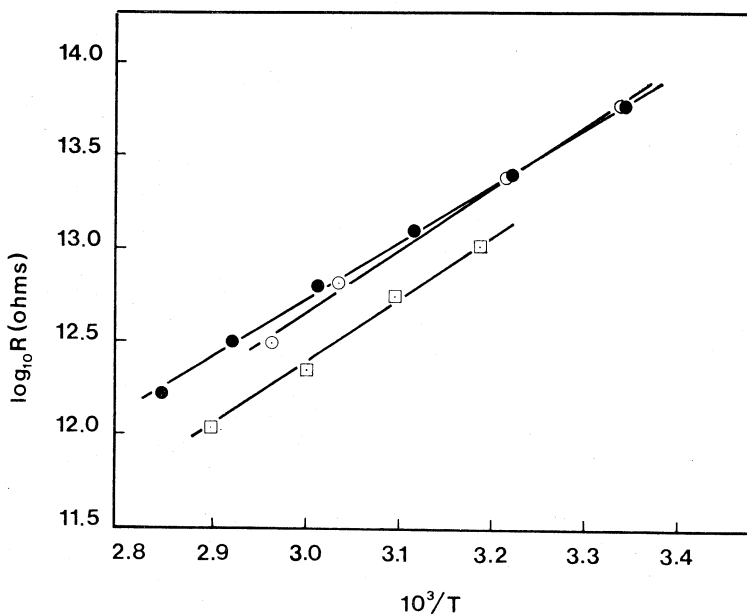


Fig. 2. - Log R against $1/T$ plot to show temperature dependence of the dark-conductivity for three different samples of selenoxanthone.

Measurements of the current were taken for every 5–10 degrees Centigrade rise in temperature. Great care was taken to ensure that thermal and conductivity equilibria had been attained in order to have a steady current, after the initial capacitative and e.m.f. surge effects, as also reported by other Authors [7–9].

The first measurement, at room temperature, was taken 2 hours after applying the external e.m.f. to the sample whilst the time interval between successive observations at higher temperatures was $1\frac{1}{2}$ hours.

Only a very slight difference was found between values obtained on the first heating cycle and those obtained on repeated cycles. Within experimental error the slope remained constant and very reproducible straight lines of log R against $1/T$ were obtained (fig. 2–4).

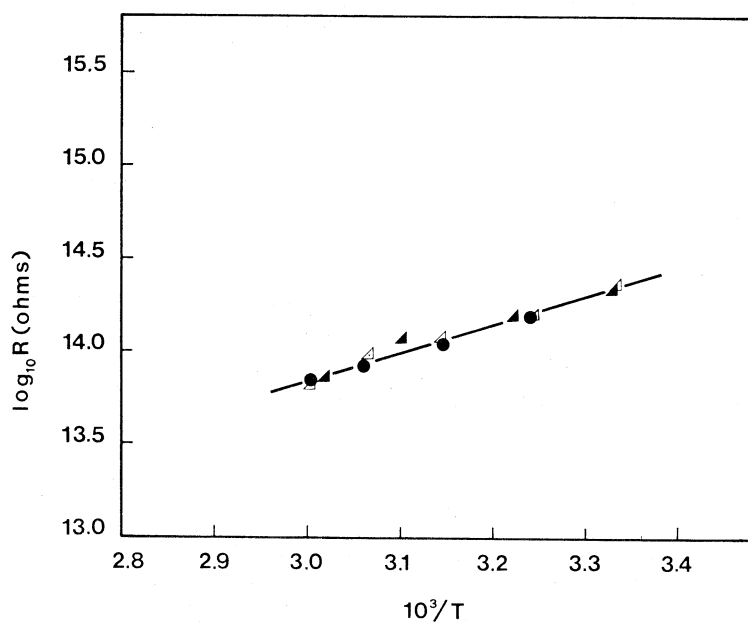


Fig. 3. – Log R against $1/T$ plot to show temperature dependence of the dark-conductivity for 1-selenochroman-4-ol: $\triangle$ first samples; $\blacktriangle$ successive run; $\bullet$ second sample.

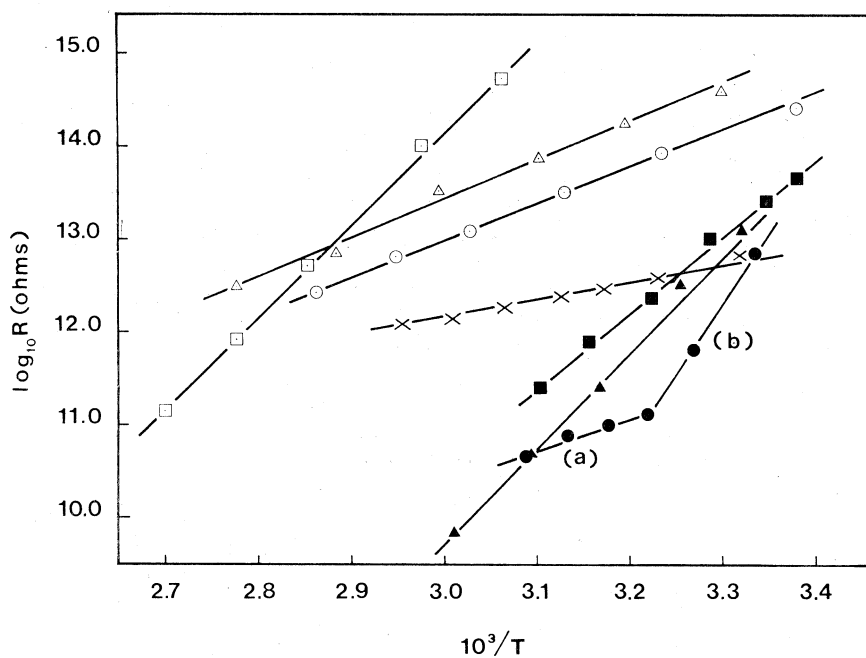


Fig. 4. – Log R against $1/T$ plot to show temperature dependence of the dark-conductivity for: $\circ$ selenoxanthene; $\square$ thioxanthene; $\triangle$ xanthene; $\bullet$ *o*-nitrobenzyl-phenyl-selenide; $\blacksquare$ *o*-aminobenzyl-phenyl-selenide; $\blacktriangle$ 1-selenochromone; $\times$ 6 H-dibenzo [*b*, *d*] selenopyran.

TABLE I
Specific Conductivity at Various Temperatures and Activation Energy of Polycrystalline Samples.

COMPOUND	M.P. (°C)	σ ($\text{ohm}^{-1} \text{cm}^{-1}$)					$\Delta\epsilon$ (eV)
		38° C	40° C	50° C	60° C	70° C	
I-selenochroman-4-ol	89°-90°	4.55×10^{-15}	5.43×10^{-15}	7.87×10^{-15}	1.11×10^{-14}	1.54×10^{-14} *	0.64
selenochromone	93°-94°	4.24×10^{-13}	1.43×10^{-12}	1.54×10^{-11}	1.40×10^{-10}	1.14×10^{-9} *	4.12
selenoxanthone	190°-191°	2.73×10^{-14}	4.10×10^{-14}	8.70×10^{-14}	1.76×10^{-13}	3.44×10^{-13}	1.32
selenoxanthene	145°	4.35×10^{-15}	7.14×10^{-15}	1.74×10^{-14}	4.00×10^{-14}	8.93×10^{-14}	1.57
thioxanthene	128°-130°	1.15×10^{-17} *	3.89×10^{-17} *	3.97×10^{-16}	3.47×10^{-15}	2.70×10^{-14}	4.03
xanthene	100.5°	2.30×10^{-15}	3.82×10^{-15}	1.01×10^{-14}	2.41×10^{-14}	5.78×10^{-14}	1.68
6 H-dibenzo [<i>b, d'</i>] selenopyran .	95°-99°	1.71×10^{-13}	2.16×10^{-13}	3.42×10^{-13}	5.21×10^{-13}	7.87×10^{-13}	0.80
<i>o</i> -aminobenzylphenylselenide . .	72°-73°	1.98×10^{-13}	5.32×10^{-13}	3.51×10^{-12}	2.07×10^{-11} *	— — — —	3.30
		25° C	30° C	35° C	— — — —	— — — —	
<i>o</i> -nitrobenzylphenylselenide . . .	62°-63°	5.43×10^{-14}	3.77×10^{-13}	2.43×10^{-12}	— — — —	— — — —	6.00
		40° C	45° C	50° C	— — — —	— — — —	
		6.76×10^{-12}	1.04×10^{-11}	1.53×10^{-11}	— — — —	— — — —	1.40

* These data were obtained by extrapolation.

(c) *Absorption spectra.*

U.V. and visible absorption spectra of evaporated films of a few micron thickness on thin quartz slab were recorded with a Perkin-Elmer 356 Spectrophotometer. A Bausch and Lomb Spectronic 505 Spectrophotometer was used for the absorption spectra of the compounds in solutions of ethanol and *n*-pentane.

RESULTS

The specific conductivity of all the substances varies with the temperature according to the Arrhenius relationship

$$(1) \quad \sigma = \sigma_0 \exp (-\Delta\epsilon/2 kT)$$

which holds for semiconductors. The graph of $\log R$ (where R is the resistance in ohm) against $1/T$ was always linear. The activation energy of the dark conductivity $\Delta\epsilon$ and the specific conductivity σ at a given temperature listed in Table I are averages over a series of measurements. $\Delta\epsilon$ were calculated from the graphs of $\log R$ against $1/T$ using eq. (1) and σ from the relationship $\sigma = J/X$, where

$$J = \frac{\text{current}}{\text{electrode area}}, \quad \text{and} \quad X = \frac{\text{applied voltage}}{\text{sample thickness}}.$$

A change in slope was observed for *o*-nitrobenzyl-phenyl-selenide for which $\Delta\epsilon$ drops from 6.0 eV to 1.4 eV for $T > 310$ K probably due to changes in electrode contact with changes in the crystal lattice and presumably in the packing factor.

The first singlet excitation energies calculated from the absorption maxima obtained from the solutions and solid films, together with the corresponding wavelengths and the calculated $\Delta\epsilon$ are listed in Table II.

TABLE II

First Singlet Excitation Energies in Solutions and in Solid Films and Thermal Activation Energies for Conduction.

COMPOUND	SOLUTION		SOLID FILM		$\Delta\epsilon$ (eV)
	λ (nm)	1E_1 (eV)	λ (nm)	1E_1 (eV)	
1-selenochroman-4-ol	254	4.88	272	4.56	0.64
selenochromone	348	3.56	351	3.53	4.12
selenoxanthone	389	3.19	383	3.24	1.32
selenoxanthene	274	4.52	282	4.40	1.57
thioxanthene	265	4.68	286	4.34	4.03
xanthene	291	4.26	295	4.20	1.68
6 H-dibenzo [<i>b</i> , <i>d</i>] selenopyran	328	3.78	324	3.83	0.80
<i>o</i> -aminobenzylphenylselenide	294	4.22	302	4.11	3.30
<i>o</i> -nitrobenzylphenylselenide	342	3.63	372	3.33	6.00 1.40

DISCUSSION

Electrode Injection Mechanism.

Our compounds show a fair degree of reproducibility for σ and $\Delta\epsilon$ (fig. 2, 3) which other Authors interpret as being indicative of intrinsic conduction, but we have evidence for a carrier injection mechanism. We shall thus discuss these molecules in terms of activation energy rather than energy gap. The $\Delta\epsilon$ values observed with one exception are all lower than the corresponding first excited singlet state energy 1E_1 (see Table II).

Attempts have already been made to correlate the energy gap value with the energies of the excited singlet or triplet states of the molecules [6, 10, 11, 12]. There have, however, always been strong theoretical objections to the validity of this sort of approach [3b, 13]; we simply consider it as a mere reference point for a general discussion.

The population of intrinsic charge carriers in semiconductors is conventionally deduced from the thermal activation energy $\Delta\epsilon$, by assuming that the observed increase in conductance upon heating is due to a free carrier generation process and that $\Delta\epsilon$ reflects an energy term characteristic of the molecular species. Thus for an organic semiconductor having for example $\Delta\epsilon = 2\text{ eV}$ the assumption of thermal carrier generation yields only about 1 carrier per 10^{17} molecules [14]. This means that the electrons and holes generated by intrinsic ionization are too few to account for the observed conduction values. In fact even with the most favourable assumptions for the effective mass and mobility of charge carriers, the equation for a narrow band semiconductor at 298 K

$$\sigma_{298} = 4 \times 10^3 \mu \exp(-\Delta\epsilon/2 kT)$$

gives a specific conductivity value of only $10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1}$ on the limit of observation [9, 16], assuming an effective mass for electrons and holes of 100, $\mu = 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (value that is about 50 fold bigger than that found for selenoxanthone [15]).

For a broad band semiconductor where the effective mass is equal to that of the free electron, $\sigma_0 = 4\mu$, the situation is even worse since σ is only $10^{-17} \text{ ohm}^{-1} \text{ cm}^{-1}$.

When we find measurable conductivity with $\Delta\epsilon$ values above 2 eV we therefore have to enquire as to the origin of charge carriers since thermal dissociation of the bulk solid provides an inadequate supply. In this case we must consider the mechanism of electrode injection of electrons and holes into the sample.

From the Richardson equation for thermionic emission [15], the number of charge carriers injected per second will amount to about 10^8 per cm^2 of electrode area. The concentration of injected carriers thus will soon exceed the thermally generated carrier concentration. We have to conclude then that

the reservoir of charge carriers available for current transport will be determined almost entirely by the nature of the contact, and the presence of adsorbed impurities and gases is responsible for modifying significantly the effective contact potential to facilitate the injection process. It is well known that donor and acceptor molecules adsorbed on the surface of organic semiconductors may greatly increase the magnitude of dark conductivity.

The fact that the energy gap may approximate to the first singlet excitation energy indicates that the energy gap for intrinsic conduction in our compounds would be so large that thermally generated concentration of holes and electrons is extremely small. Under these conditions, the mere attachment of electrodes to the material, or the presence of impurities at the surface or surface states, can introduce more charge carriers at a greater rate into the insulator than can be generated intrinsically. So dark conductivity in the examined aromatic compounds seems very likely to be an extrinsic process where the electrons and/or holes carrying the current in the solids must have arisen from injection by the electrodes. Since there is experimental evidence that $\Delta\epsilon$ is independent of the work function of the metallic electrode [17-19] the simple theory of carrier injection requires some modification. This is done by assuming the presence of surface states on the solids which serve to create a potential barrier at the semiconductor surface which remains unchanged on making the metal contact [12, 17]. For instance the presence of oxygen molecules, which is rigorously excluded only at strongly rarefied atmosphere of say 10^{-7} torr²⁰, giving rise to surface states will play a dominant role as an electron trap at the crystal surface, facilitating hole injection. Similarly traces of adsorbed water lower $\Delta\epsilon$ very strongly through protonic conduction [12]. In this way it is possible to explain why $E_{inj} = \Delta\epsilon/2$ is less than $E_g/2$, the true energy gap.

An analysis of the results listed in Tables I and II leads us to some conclusions. The anomalously low $\Delta\epsilon$ for 1-selenochroman-4-ol and 6-H-dibenzo [*b*, *d'*] selenopyran and the consequent discrepancy between the observed $\Delta\epsilon$ and the optical excitation energy, seems very likely to be due to traces of adsorbed water. An increase in temperature will tend to decrease the surface coverage of adsorbed water, but it will also tend to cause an increased ionization of the surface states, thus lowering the activation energy for carrier injection. Protonic conduction seems to be a distinct possibility in these two compounds in view of the observed dependence of the current upon time. Moreover for 1-selenochroman-4-ol there is the possibility of the formation of intermolecular hydrogen bonds between the hydrogen of the OH groups.

For 1-selenochromone, *o*-aminobenzyl-phenyl-selenide and thioxanthene, where $\Delta\epsilon$ approximates to 1E_1 , a few electron donor surface states just above the Fermi level donate some electrons into the conduction band and a positive charge builds up by compensation on the semiconductor surface [9, 12]. The bands bend down at the surface and on making the contact we force an increasing positive charge barrier layer (fig. 5). This leads to

a straightening of the bands, with the possibility that $\Delta\epsilon \simeq E_g$ and electron and hole injection should occur in opposite directions at equal values of $\Delta\epsilon$ and therefore at equal rates.

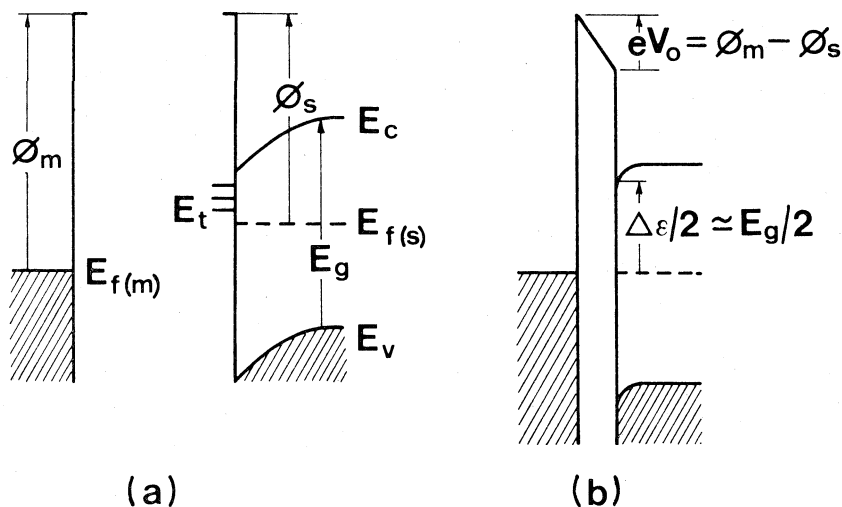


Fig. 5. - To show how $\Delta\epsilon \simeq E_g$: (a) metal-semiconductor surface potential not at equilibrium with a low number of surface states E_t ; (b) after equilibration, surfaces in contact. - ϕ_m thermionic work function of metal; ϕ_s thermionic work function of semiconductor; E_g energy gap between top of valence band E_v , bottom of conduction band E_c ; $E_{F(m)}$ Fermi level of metal and $E_{F(s)}$ for semiconductor; eV_0 contact potential.

O-nitrobenzyl-phenyl-selenide shows a change in slope (fig. 4). The conductivity is extrinsic in both portions (a) and (b) and the change of slope reflects a change in the packing and in the crystal lattice near the melting point, as a result of which conduction proceeds by a different mechanism. The value of 6.0 eV might correspond to some situation such as hole injection with a complete trapping of the electronic current and the great volatility of these crystals makes it reasonable to assume that electron accepting levels are associated with molecular vacancies on the organic crystal surface. These vacancies will increase as the temperature is raised and hence give rise to increased band bending and consequently to the lowering of $\Delta\epsilon$.

INFLUENCE OF STRUCTURE

On examining the series: selenoxanthone, selenoxanthene, thioxanthene, and xanthene, we can see a trend in the $\Delta\epsilon$ and σ values.

Selenoxanthone shows the lowest $\Delta\epsilon$ and the highest σ compared with the other three compounds. The $>C=O$ group of selenoxanthone increases the conjugation scheme promoting the delocalization of the π -electrons in the molecule which favours conductivity while the $>C=H_2$ group of selenoxanthene between two aromatic rings interrupts the conjugation scheme

since the $>C=H_2$ electrons are not delocalized. The presence of the selenium atom in these two compounds seems to influence positively the specific conductivity and lowers the $\Delta\epsilon$ because of the stronger metallic character of selenium compared to sulphur.

The high $\Delta\epsilon$ found for thioxanthene is in close agreement with the value of 1E_1 and that could lead us to accept an intrinsic conductivity for this compound. Calculation using equation (1) with $\sigma_0 = 4 \times 10^3 \mu$ and $\mu = 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, gave a specific conductivity at 313 K, of the order $10^{-22} \text{ ohm}^{-1} \text{ cm}^{-1}$ much lower than that measured experimentally. We thus suggest the mechanism previously proposed for the compounds having $\Delta\epsilon \simeq ^1E_1$.

CONCLUSION

We conclude that conduction in the aromatic compounds examined here mainly arises by charge carrier injection and this accounts for the high σ values found and for the observed $\Delta\epsilon$ being lower than 1E_1 . Conductivity in compressed powders is essentially surface type. The carriers move predominantly on the surface where they concentrate due to the presence of traps [9, 21].

At this stage further work would be particularly useful on surface states, surface potential, electric field distribution inside the sample, Hall mobilities and carrier detrapping by electric fields.

The presence of selenium in the molecule plays an important role in increasing the conductivity through delocalization of electrons, but functional groups have a greater influence on the activation energy and conductivity than the hetero-atoms, as can be seen from the U.V. spectra for the $S_0 \rightarrow S_1$ transition [22].

Acknowledgements. The Authors wish to thank Prof. G. Semerano for helpful discussions and advice, and Prof. J. Degani for the supply of the organic selenium derivatives.

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