

## FURTHER STUDIES ON SEMICONDUCTIVITY IN CORRELATION WITH THE OPTICAL PROPERTIES OF SOME RELATED SOLID CHARGE-TRANSFER COMPLEXES FOR THEIR POSSIBLE APPLICATION IN SOLAR CELLS

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### ABSTRACT

Several charge-transfer (CT) complexes have been prepared by (1:1) reactions of nitrobenzene derivatives (acceptors) with anil and anil derivatives (donors), recrystallized from the appropriate solvent and dried over  $P_2O_5$ . The electron affinities ( $E_A$ ) and ionization potentials ( $I_P$ ) have also been evaluated, from optical measurements, for the investigated acceptors and donors, respectively. Furthermore, the temperature dependence of the direct-voltage electrical conductivity has been extensively investigated in the solid state, correlated with  $E_A$  and  $I_P$ , and discussed in detail.

### INTRODUCTION

A completely satisfactory theory of organic conduction has not yet emerged. The picture is taking shape, however, and it is clear that electrical properties are dictated by the molecular nature of organic solids.

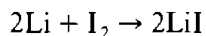
Charge carriers are most readily formed by the activation of nonbonding or  $\pi$ -bonded electrons; if they are delocalized in a conjugated system, they form an internal conduction path of high mobility. Thus, long conjugated systems form one class of organic conductors. Also,  $\pi$ -bonded electrons give a better intermolecular orbital overlap than  $\sigma$ -bonds. Hence, it has been established that planar aromatic molecules that stack like cards with an interplanar spacing no greater than that in graphite, provide a conduction pathway normal to the molecular planes. Thus, a major class of organic conductors includes stacked-planar  $\pi$ -electron systems.

Partial formation of radical ions may occur in the donor-acceptor interac-

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tion leading to charge-transfer (CT) complexes that form rigid stacks; these stacks determine the mechanical properties of the solid complexes. In this case, the conductivity is highly anisotropic and occurs by radical-ion disproportionation as suggested by Eley [1]. Generally, these polymeric CT complexes are brittle materials. They are, however, of value where mechanical properties are not important, as in the case of the poly-(2-vinylpyridine)iodine complex used as a cathode in the miniature Li-I<sub>2</sub> primary cell made by Wilson Greatbatch Ltd. [2] for implantable cardiac pacemakers. The complex serves a dual function: as a source of iodine for the cell reaction



and as an electronic conductor carrying the current to the cell collector. Herein, it is of great interest to note that the conductivity of the complex is constant at  $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$  as the iodine concentration falls from 90 to 75% on discharging the cell. This solid-state cell with the LiI electrolyte formed in situ has a very high energy density ( $120 \text{ W h kg}^{-1}$ ) compared with the best lead-acid battery available ( $30 \text{ W h kg}^{-1}$ ) and has a service life of ten years, thus illustrating the use of one commercially valuable conducting polymer.

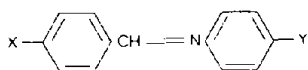
Alternatively, such materials may prove useful for the storage of chemical energy. The present investigation was carried out to evaluate the electrical and optical properties of some selected CT complexes capable of being mass produced economically from naturally occurring sources or from cheap starting materials. Our aim was to determine their suitability and efficiency for solar-energy storage.

## MATERIALS AND METHODS

### *Starting materials and sample preparation*

The acceptors used were of pure chemical grade (AR) supplied by BDH. The donors used were prepared from pure chemicals (BDH); their identities were established by both chemical analysis, m.p. determination and IR absorption spectra. The solid CT complexes were prepared directly from their corresponding ethanolic solution of acceptors and donors.

Experimental details for the preparation of the CT complexes (donor/acceptor = 1:1) were followed as previously described [3,4] with some modifications for sample purification and recrystallization. The donors used have the following structural formula:



a, X = H, Y = H; f, X = N(CH<sub>3</sub>)<sub>2</sub>, Y = H; i, X = H, Y = N(CH<sub>3</sub>)<sub>2</sub>; j, X = Y = N(CH<sub>3</sub>)<sub>2</sub>.

The acceptors encountered in the present study are picric acid, picryl chloride and trinitrotoluene.

#### *Electronic absorption spectra measurements*

These were carried out in an ethanolic solution, in the solid state, mullied in Nujol (220–700 nm) using a Pye Unicam SP 8000 spectrophotometer at room temperature (25°C).

#### *Determination of electron affinity ( $E_A$ ) and ionization potential ( $I_p$ )*

These were estimated from their corresponding electronic spectra using a calculation analysis method previously reported [5–7] for other CT materials.

#### *DC electrical conductivity measurements*

The conductivity measurements were carried out [8] on the investigated samples using a DC electrometer (type TR-150 I Orion-K.T.V., Budapest). A silica tube holder or conductivity cell was used. The silica tube was provided with a ground joint to be connected to a detachable head through which one electrical lead passed by way of a silica-sealed tungsten rod. On the opposite side of the tube, a second lead was spot-welded and sealed in glass via a tungsten rod. The two electrodes were made of platinum. The conductivity cell, with the specimen inside, could be evacuated to  $10^{-3}$  mm Hg by means of an upper tube built into the ground joint and connected to a high-vacuum system.

The samples used in the measurements were pressed into cylindrical pellets at a pressure of about  $300 \text{ kg cm}^{-2}$ . This pressure was chosen as the electrical conductivity was independent of the load. The measurements were taken often, at 15-min intervals, for each temperature equilibration in the investigated range (293–473 K).

All of the above measurements were checked several times; in each case, good reproducible data were obtained.

## RESULTS AND DISCUSSION

Tables 1 and 2 give the electron affinities,  $E_A$  (eV), and ionization potentials,  $I_p$  (eV), determined for the acceptors and donors investigated. These were evaluated from electronic spectral measurements (using the solid technique) following the method and calculations of Briegleb and Czekalla [6]. It is clear from Tables 1 and 2 that: (1) the electron affinity ( $E_A$ ) of the

TABLE 1

Chemical nomenclature and identification of donors, acceptors and their corresponding CT complexes

Donors		Acceptors		CT complexes
Symbol	Nomenclature	Symbol	Nomenclature	
a	Anil (benzilidine aniline Schiff base)	I	Picryl chloride	I <sub>a</sub>
f	<i>para-N</i> -Dimethyl anil (aldehyde subst.)			I <sub>f</sub>
i	<i>para-N</i> -Dimethyl anil (aniline subst.)			I <sub>j</sub>
j	<i>para</i> -Dimethyl <i>N,N'</i> -anil	II	Picric acid	II <sub>a</sub> II <sub>f</sub> , II <sub>i</sub> , II <sub>j</sub>
		III	Trinitro- toluene	III <sub>i</sub>

acceptors was found to decrease in the order: picryl chloride > picric acid > trinitro toluene. This observation correlates with the increased steric effect of the molecule, which propagates in the same direction; (2) the ionization potential ( $I_p$ ) of the donors seems to decrease in the order anil > mono-*para*-substituted *N*-dimethyl anil > di-*para*-substituted *N,N'*-dimethyl anil. This decrease is plausibly correlated with the increased electron density and greater polarizability of the donor molecules, which would facilitate the ionization process. This is due to the electron-repelling nature of the CH<sub>3</sub> group.

Figures 1–3 represent the variation of DC electrical conductivity as a function of temperature for solid-state samples consisting of substituted anil, anil donors and their corresponding CT complexes with the substituted trinitrobenzene acceptors.

With the exception of the CT complex of *para-N*-dimethyl anil with picryl chloride, there is a positive temperature coefficient of electrical conductivity ( $d\sigma/dT$ ) for all curves. Thus, all but one of the specimens investigated have

TABLE 2

Values of the  $E_A$  and  $I_p$  values obtained for the trinitrobenzene acceptors and anil or substituted anil donors investigated, respectively

Acceptors		Donors	
Compound	$E_A$ (eV)	Compound	$I_p$ (eV)
I	1.0	a	7.22
II	0.70	f	7.56
III	0.60	i	7.17
		j	7.15

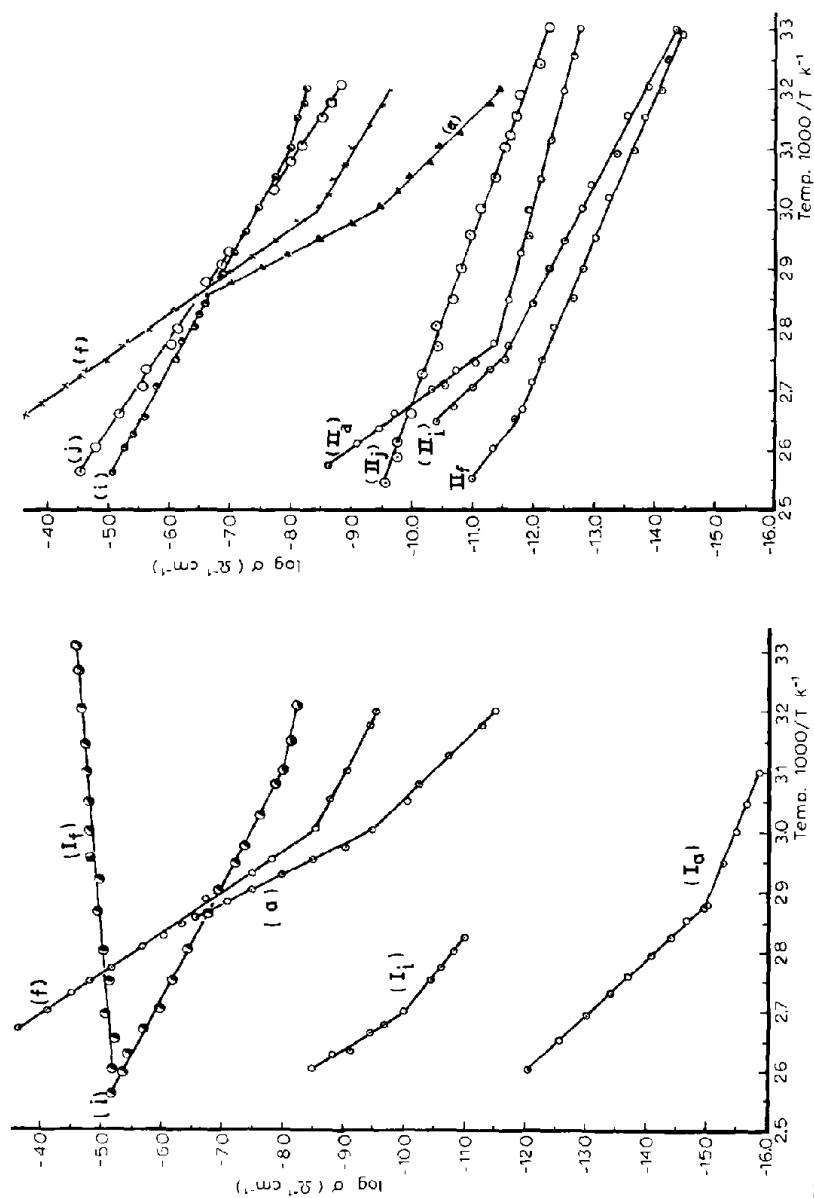


Fig. 1. The variation of electrical conductivity as a function of temperature for CT complexes derived from a picrylchloride (I) acceptor with substituted anil donors.

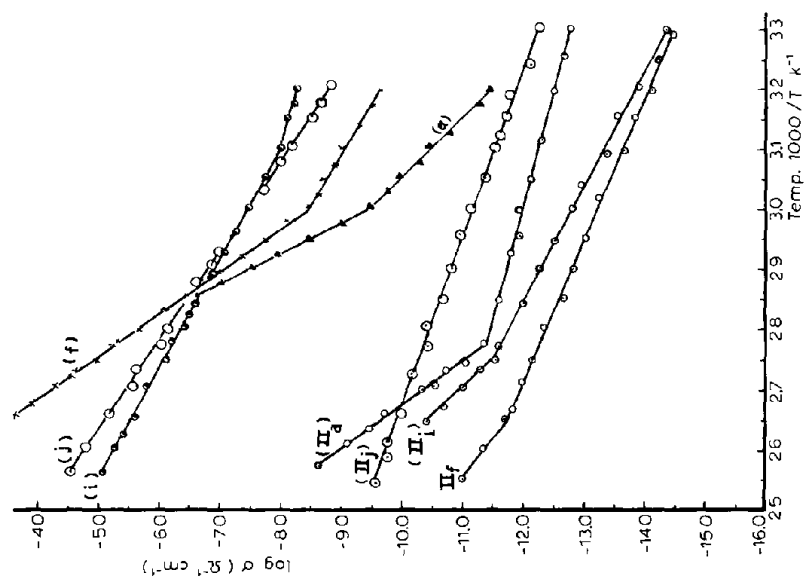


Fig. 2. The variation of electrical conductivity with inverse temperature for CT complexes derived from a picric acid (II) acceptor with substituted anil donors.

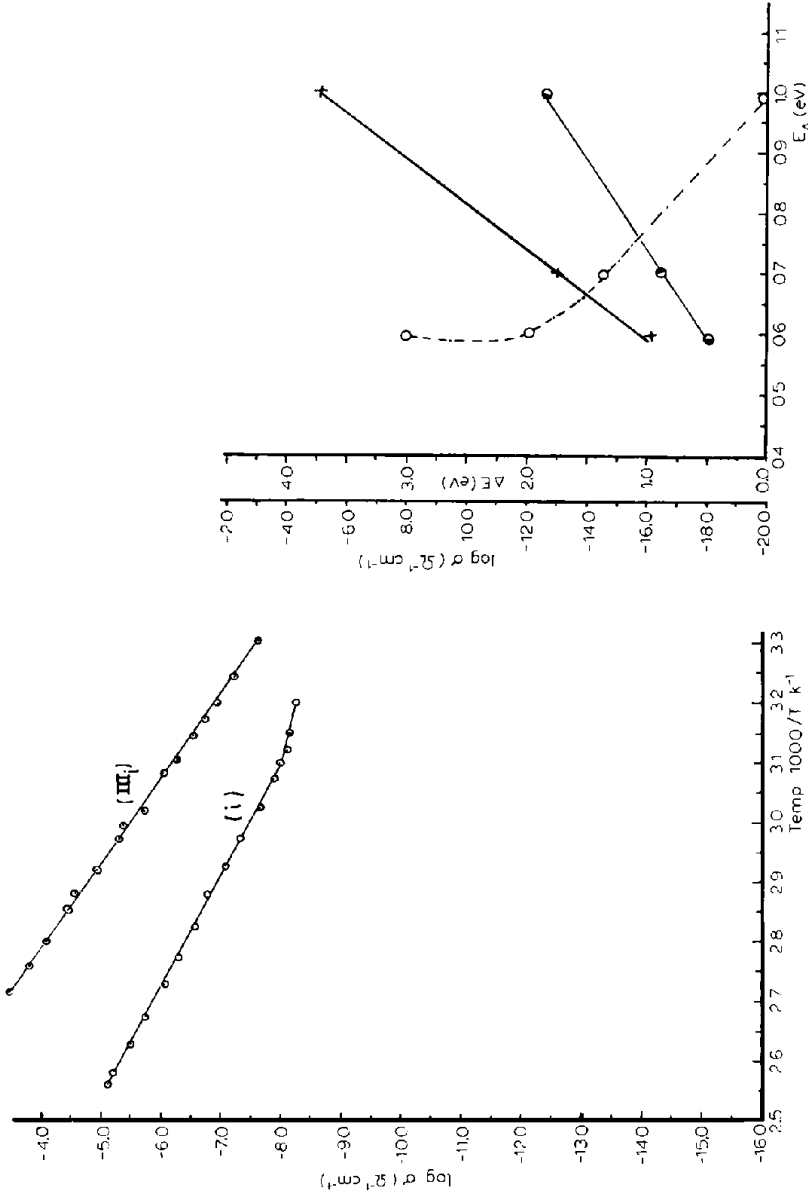


Fig. 3. Values of electrical conductivity as a function of temperature for CT complexes derived from a trinitrotoluene (III) acceptor with an anil donor.

Fig. 4. The variation of electrical conductivity ( $\log \sigma_{25}$  ( $\Omega^{-1} \text{ cm}^{-1}$ )) and activation energies for conduction ( $\Delta E_c$  (●),  $\Delta E_a$  (○), eV) as a function of the electron affinity of the acceptors for trinitrobenzene CT complexes with *p*-*N*-dimethyl anil.

a semiconducting character in the temperature range investigated. In the case of the *para-N*-dimethyl anil CT complex with picryl chloride (Fig. 1, curve I<sub>f</sub>), the material possesses a negative temperature coefficient of electrical conductivity ( $d\sigma/dT$ ), typical of a metallic conduction mechanism possessing a relatively high specific electric conductance.

The conductivity of the semiconducting samples varies exponentially with temperature according to the well-known equation [9]

$$\sigma = \sigma_0 e^{-\Delta E/RT} \quad (1)$$

where  $\sigma$  is the electrical conductivity at a given temperature  $T$ ,  $\sigma_0$  is the pre-exponential factor,  $\Delta E$  is the activation energy for conduction, and  $R$  is the Boltzmann constant. From this linear relationship, the activation energy,  $\Delta E$ , could be calculated (see Table 3). The  $\Delta E$  values can be interpreted by a band model containing a partially occupied set of trap states near the centre of the energy gap between valence ( $\pi$ ) and conduction ( $\pi^*$ ) bands.

It is difficult to calculate the band structure of such CT complexes with sufficient accuracy, since we are awaiting the future full development of the origin of these bands. Two common distinct transport mechanisms are the most likely to be considered herein: band conduction and thermally activated hopping conduction due to the relatively weak electronic coupling between the organic molecules. The role of acceptors is to facilitate and enhance the  $\pi$ -electron delocalization and hence the process of electrical conduction, thus minimizing the value of  $\Delta E$ . In CT complexes, the partial formation of radical ions is likely to occur in the donor-acceptor interactions leading to CT complexes which form rigid stacks which determine the final mechanical

TABLE 3

Values of the measured activation energy (eV) for conduction and the energy gap (eV) for the investigated donors and their corresponding CT complexes with substituted trinitrobenzene acceptors

Donors			CT complexes				
Compound	Activation energy (eV)		Energy gap, $E_g$ (eV)	Complex	Activation energy (eV)		Energy gap, $E_g$ (eV)
	$\Delta E_c^a$	$\Delta E_i^b$			$\Delta E_c^a$	$\Delta E_i^b$	
a	1.80	3.50	7.00	I <sub>a</sub>	0.99	2.05	4.10
f	1.40	2.68	5.40	I <sub>f</sub>	0.25	0.50	1.00
i	0.45	0.85	1.70	I <sub>j</sub>	1.80	3.72	7.44
j	0.70	1.40	2.80	II <sub>a</sub>	0.50	1.0	2.00
				II <sub>f</sub>	0.90	2.00	4.00
				II <sub>i</sub>	0.70	1.40	2.80
				II <sub>j</sub>	1.80	3.50	7.00

<sup>a</sup> Extrinsic activation energy.

<sup>b</sup> Intrinsic activation energy.

properties of the resultant solid complexes. Thus, conductivity is highly anisotropic and occurs by radical-ion disproportionation [1].

From Table 3 and Figs. 1–5, it is of significance to note the following points.

(1) For donors, the electrical conductivity increases and both activation energies and the energy gap decrease on going from anil via *para-N*-dimethyl anils (ald. subst.) via *para-N'*-dimethyl anils (aniline subst.) to *para-N,N'*-dimethyl anils. This could probably be explained on the basis of the increased electron density and polarization of the donor molecule as a function of substitution mode and magnitude. Thus, this may facilitate the ionization mechanism and electron flow leaving behind electronic and/or ionic conduction mechanisms to take place. Thus, results of the spectrophotometric determination of  $I_p$  and conductivity measurements are in conformity.

(2) As a result of complexation, the electrical properties display a general trend, namely an increase of the electrical conductivity and a decrease of the activation energy and energy gap for the conduction process. This is most probably attributed to the increased number and mobility of charge carriers which are most readily formed by the activation of non-bonding or  $\pi$ -bonded electrons [10]. Since they are delocalized in a highly conjugated system, they form an internal conduction pathway of high mobility. Thus, when there are an increased number of charge carriers as a function of temperature, the

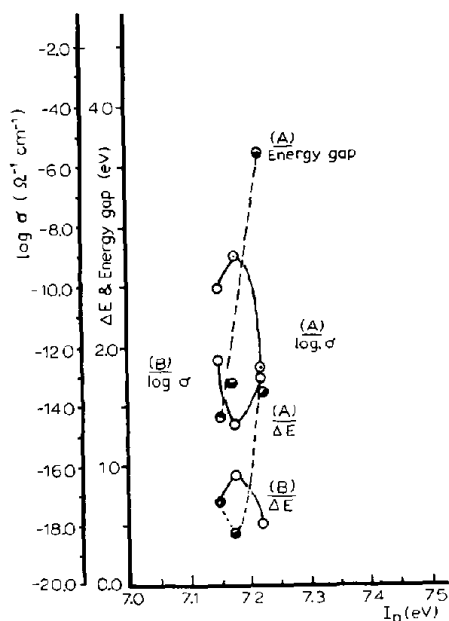


Fig. 5. The variation of electrical conductivity ( $\log \sigma_{25}$ , by extrapolation), activation energy for conduction and energy gap as a function of ionization potential ( $I_p$ ) of anil donors (A); and the same relation for their corresponding CT complexes (B) with picric acid.



mobility decreases and the metallic conduction mechanism predominates (see Fig. 1, curve  $I_f$ ). The latter behaviour (metallic) could probably be explained by the occurrence of some kind of molecular association in the solid state which permits their further approach through  $n-\pi^*$  and  $\pi-\pi^*$  electronic transitions as depicted from our extensive studies [11] on some CT complexes. Thus, we can say that long conjugated systems form one class of organic conductor. Also,  $\pi$ -bonded electrons give better intermolecular overlap than  $\sigma$ -bonds. Alternately, it is suggested [10] herein that the excited orbitals of  $\pi$ -electrons in the isolated molecules overlap to give a non-localized orbital stretching throughout the whole crystals. This investigation was originally stimulated by the suggestions of Gyorgi [12], Vartanian [13] and Abou Sekkina and Abou El-Enein [10].

Very few exceptional cases are also encountered (see Fig. 1, curve  $I_i$  and Fig. 2, curve  $II_i$ ) which have a reversed nature. This means that the activation energy and energy gap of some of the investigated donors increase slightly through complexation and this is probably correlated with the probable thermal decomposition of the complex on heating during conductivity measurements. Evidence supporting this view is their relatively high electrical conductivity in the moderate temperature range.

Since the activation energy of conduction is doubled at higher temperature in most cases (see Table 3 and Figs. 1–5), the investigated materials pass from an extrinsic conduction mechanism to an intrinsic conduction mechanism. The inversion (knee) temperature was found to be highly dependent on the impurity content of the materials investigated and their previous thermal history. This was in conformity with our previous investigation and supported the suggested molecular structure of the CT complexes [11]. The extrinsic conduction evolves from deep donor centres.

Accordingly, promising results were obtained which were in conformity and support previous deductions.

## CONCLUDING REMARKS

This work on organic semiconduction has not failed. It has succeeded in showing that the first step forward must be to understand the organic metallic state. The second step comes as a challenge to unravel the relationship between charge-carrier mobility and the molecular structure of organic semiconductors. This is most important. Then, as the third step, based on the results obtained, we will be able to make organic complexes which have metallic conductivity and very small energy gaps (in most cases). This enables us to examine some of these CT complexes for their light energy exposure, to measure and store the generated photoelectric current at a profit (economical mass production) for their final industrial application in solar energy storage (solar cells). These constitute the major goals of our

future research work. The results obtained support the idea that the application of some such materials in solar cells will be realized. Science, however, must come before technology.

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