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ELECTRICAL PROPERTIES OF CHARGE TRANSFER COMPLEXES OF DIAMINONAPHTHALENE DONORS WITH DINITRO- AND TRINITROBENZENE ACCEPTORS

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ABSTRACT

The electrical properties of some charge transfer complexes, with stoichiometries 1 : 1 and 1 : 2 (donor : acceptor), of 1,5-diaminonaphthalene and 2,3-diaminonaphthalene with dinitro- and trinitrobenzenes have been investigated. The positive temperature coefficient of electrical conductivity ($d\sigma/dT$) is evidence for a semiconducting character. The energy gaps (E_g) for conduction and the charge transfer excitation energies (E_{CT}) have been discussed. The mechanism of the conduction process is also interpreted.

INTRODUCTION

A remarkable aspect of organic systems which in their pure state have very high resistivities, is that some of them show enormous increases in conductivity when mixed with each other to form molecular complexes [1]. The conductivity of these solid molecular complexes is measured to provide information concerning the extent to which the components are polarized as a result of intermolecular interactions. Most notable are the charge transfer (CT) complexes and the closely related radical ion systems [1–5]. Conductivities in the order of 10^{-9}–10^{-12} Ω^{-1} cm^{-1} have been reported for a relatively large number of CT complexes, but a value of 1.3 Ω^{-1} cm^{-1} for perylene–I_2 has also been reported [6]. The most thoroughly studied and highly conducting compounds are those containing tetrathiofulvalene (TTF) and related donors, and tetracyanoquinonedimethane (TCNQ) which have conductivities in excess of 10^2 Ω^{-1} cm^{-1} [7]. Recently, the electrical properties of CT complexes of trinitrobenzenes with substituted Schiff bases were studied in an attempt to validify their possible application in solar-energy storage [8].

The study reported in the present article deals with the electrical conductivities, current–voltage characterstics and optical properties of CT complexes of 1,5-diaminonaphthalene and 2,3-diaminonaphthalene with di- and trinitroaromatic acceptors. These investigations may yield a material of semiconducting properties which may find an application in solar cells as energy convertors.

EXPERIMENTAL

The materials used in the present investigation were pure laboratory grade chemicals (BDH). The donors were (a) 1,5-diaminonaphthalene and (b) 2,3-diaminonaphthalene. The acceptors were (1) picric acid, (2) 1,3,5-trinitrobenzenes (3) picryl chloride, (4) 3,5-dinitrobenzoic acid, (5) 3,5-dinitrosalicylic acid, (6) 2,4-dinitrophenol and (7) 1,3-dinitrobenzene. The preparation of CT complexes and their elemental analysis, m.p., UV, IR and NMR analysis are described elsewhere by Ayad [9]. The electronic absorption spectra were measured in the solid state as a Nujol mull using a Unicam SP 8000 spectrophotometer.

The electrical conductivity and the current–voltage (I–V) measurements were made on a Super Megohmmeter (Model RM 170) electrometer. The samples were pressed into discs of 13 mm diameter and 2–3 mm thickness at a pressure of about 700 kg cm^{-2}. The surfaces of the discs were painted carefully with a silver paste. The temperature was measured in air using a Cu/CuNi Comark thermometer placed close to the sample.

RESULTS AND DISCUSSION

The electrical conductivities (Ω^{-1} cm^{-1}) for various 1 : 1 (D : A) CT complexes of the donors (a) and (b) with the different acceptors were measured. In addition, the measurements were also carried out for some 1 : 2 (D : A) complexes. Figures 1 to 4 illustrate the variation in log σ as a function of the reciprocal of temperature ($1/T$) in accordance with the following equation.

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

where σ is the electrical conductivity at a given temperature T, σ_0 is the initial conductivity (the pre-exponential factor), ΔE is the activation energy of conduction and K is the Boltzmann constant. The activation energy values are deduced and listed in Table 1.

Because there is a positive temperature coefficient of electrical conductivity ($d\sigma/dT$) for each curve, all the CT complexes are considered to be among those organic compounds that are semiconducting. It can also be shown that phase transitions occurred in all complexes under the influence of temperature, but the CT complex of donor (b) with trinitrobenzene, with a stoichiometry of 1 : 2, has only one regime of conduction. For most CT

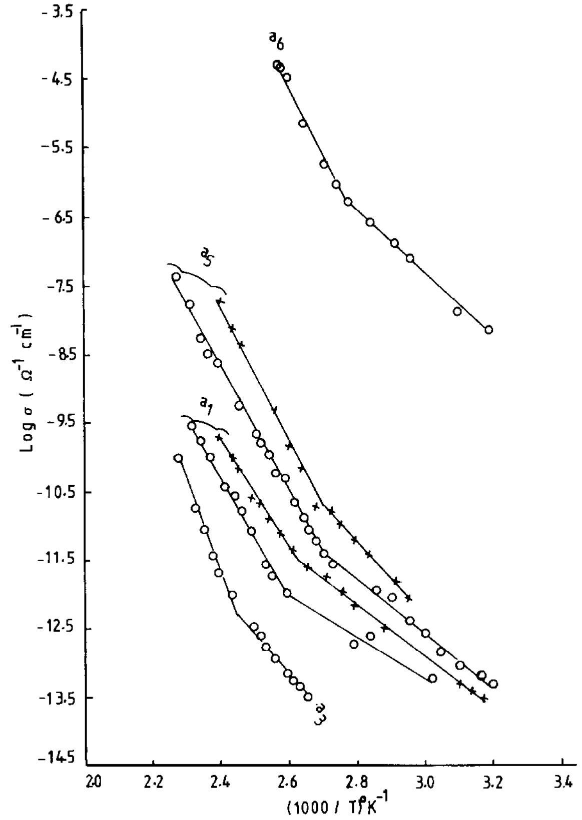

Fig. 1. Temperature dependence of the electrical conductivity of 1 : 1 CT complexes of 1,5-diaminonaphthalene with acceptors (1), (3), (5) and (6), on heating (o) and cooling (×) cycles.

complexes, the activation energies for each regime in the temperature conductivity profiles were obtained from heating as well as cooling cycles. Values of the activation energies for each regime of conduction during cycles of heating and cooling are reasonably comparable. This behaviour would ensure that no chemical interaction takes place between the partners of the CT complexes under investigation. The phase transition phenomena in the temperature range 51–58 °C can be attributed to a change in the type of packing and to a volume change. The existence of segregated stacks of donors and acceptors along a particular crystallographic direction is evident in the CT complexes of stoichiometry 1 : 1 [10]. This is necessary but not sufficient to achieve metallic conductivity. Accordingly, the electrical properties of these materials are highly anisotropic, with the conductivity along the molecular stacks being appreciably higher than that normal to the arrays [6]. The tendency for stacking is consistent with the maximum space-filling and the maximization of the degree of nonbonding interactions. The stabilization of stacks can be partially rationalized by noting that good nearest-

TABLE 1

Values of the activation energy (ΔE), energy gap (E_g) and the transition temperature (T_s) for 1:1 and 1:2 CT complexes of donors (a) and (b) with different acceptors, measured during heating and cooling cycles

Acceptor	Ratio	Heating cycles				Cooling cycles			
		ΔE_1 (eV)	ΔE_2 (eV)	E_g (eV)	T_s (°C)	ΔE_1 (eV)	ΔE_2 (eV)	E_g (eV)	T_s (°C)
Complexes with 1,5-diaminonaphthalene									
(1)	1:1	0.621	1.739	3.478	113	0.749	1.65	3.30	114
	1:2	0.719	1.247	2.494	98	0.879	1.253	2.506	102
(2)	1:1	0.445	1.361	2.72	105	0.593	1.097	2.194	115
(3)	1:1	1.111	1.881	3.76	142				
	1:2	0.483	2.006	4.132	157	0.472	2.111	4.222	158
(4)	1:1	0.734	1.805	3.61	115	0.605	1.381	2.762	120
(5)	1:1	0.849	1.791	3.582	97	1.061	1.90	3.80	97
	1:2					0.960	1.305	2.610	88
(6)	1:1	0.908	1.942	3.883					
Complexes with 2,3-diaminonaphthalene									
(1)	1:1	0.705	2.089	4.179	68				
	1:2	0.825	1.518	3.036	97	0.812	1.677	3.354	97
(3)	1:1	0.99	1.904	3.807	51				
	1:2		1.337	2.674			1.416	3.232	
(4)	1:1	0.842	1.98	3.96	113				
(5)	1:1	1.114	2.088	4.176	56				
	1:2	0.623	1.579	3.158	106	0.60	1.751	3.502	106
(6)	1:1	0.842	2.202	4.04	53				
(7)	1:1	0.879	2.121	4.242	83				

neighbour overlap of the delocalized π-electrons is provided by tilting the molecular plane relative to the stacking axis [11]. Consequently, an increase of the electrical conductivity and a decrease of the activation energy gap would be observed. In addition, it can be seen from Table 1 that the activation energies (ΔE_1 and ΔE_2) for the CT complexes of donor (a) are generally close to the corresponding values for CT complexes of donor (b).

The crystal packing conditions which would have a more pronounced influence on the conductivity can be observed by studying the electrical conductivity of 1:2 (D:A) complexes of donors (a) and (b) with acceptors (1), (3) and (5). In these complexes, the stacking sequences are different from those having a 1:1 ratio. The plots of log σ against $1000/T$ are shown in Figs. 2 and 4. It can be shown that these complexes also have a semiconductor behaviour. The values of ΔE for each regime of conduction during cycles of heating and cooling are listed in Table 1 together with the transition temperatures (T_s). For each cycle, the values of ΔE are in close agreement. However, the activation energies, especially ΔE_2, are higher than those for the corresponding complexes having a 1:1 ratio. This is most

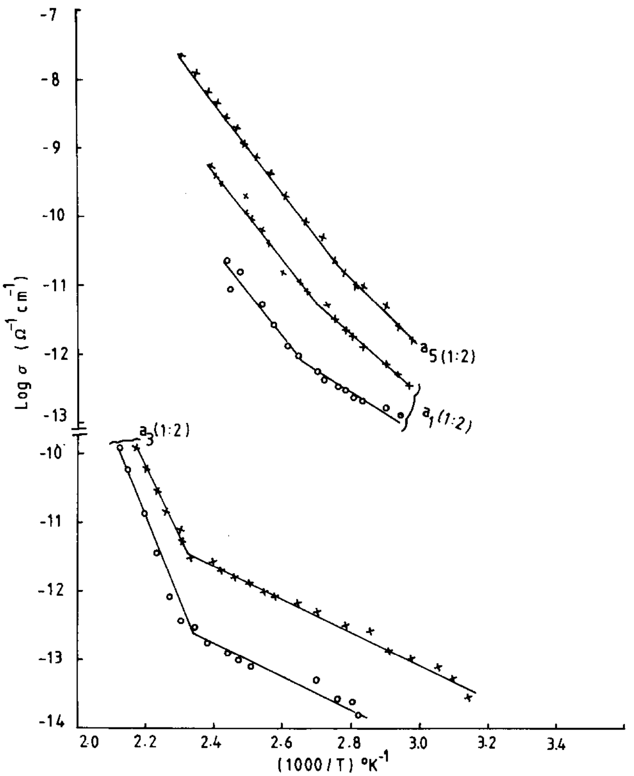

Fig. 2. The temperature dependence of the electrical conductivity of 1:2 CT complexes of 1,5-diaminonaphthalene with acceptors (1), (3) and (5), on heating (o) and cooling (×) cycles.

TABLE 2

Experimental CT energy E_{CT}, electron affinity E^{A} and δ values for 1:1 CT complexes of 1,5-diaminonaphthalene with acceptors (1)–(7)

Acceptor	E^{A} (eV)	E_{CT} (eV)	δ (eV)
(1)	0.7 [a]	2.64	0.65
(2)	1 [a]	2.54	0.16
(3)	0.6 [a]	2.70	1.05
(4)	0.57 [b]	2.44	1.17
(5)	0.53 [b]	2.30	1.28
(6)	0.5 [a]	2.76	1.23
(7)	0.3 [a]	2.70	

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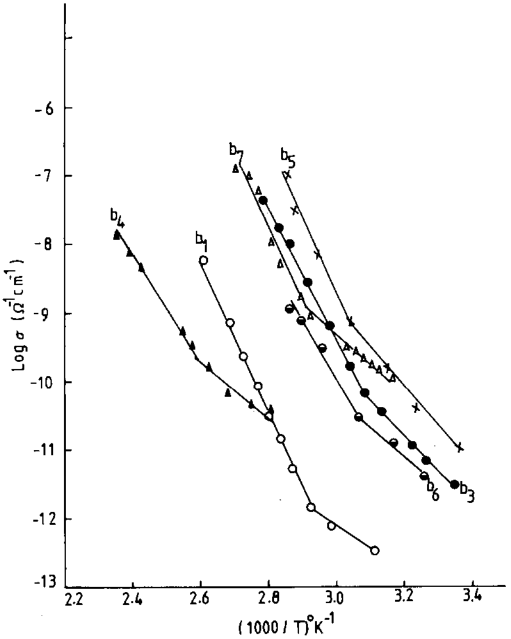

Fig. 3. The temperature dependence of the electrical conductivity of 1 : 1 CT complexes of 2,3-diaminonaphthalene with acceptors (1), (3), (4), (5), (6) and (7) on heating cycles.

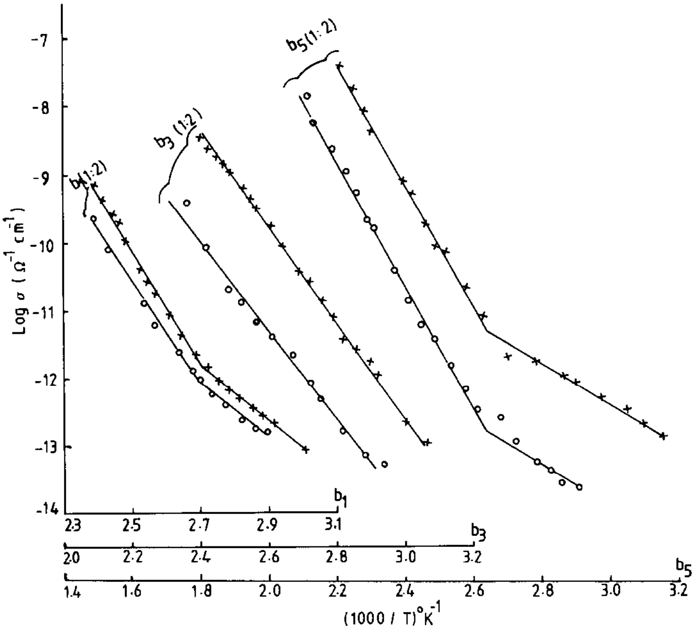

Fig. 4. The temperature dependence of the electrical conductivity of 1 : 2 CT complexes of 2,3-diaminonaphthalene with acceptors (1), (3) and (5), on heating (o) and cooling (×) cycles.

probably attributable to the change in the alternate stacking of the donor with the acceptor molecules. Therefore, the nearest-neighbour interaction would be destabilized and, consequently, a less delocalized π-electron would be favoured.

The electronic absorption spectra for the 1 : 1 CT complexes of donor (a) with all the acceptors were measured; a band was observed which does not exist in the spectra of pure donor or acceptor. The charge transfer excitation energies, E_{CT} (eV), were calculated and are listed in Table 2. It can be shown that the values of the energy gaps, E_g, for these complexes are higher than those of charge transfer excitation energies. Kuroda et al. [3] in their investigation of a series of complexes of 1,3,5-trinitrobenzene with aromatic hydrocarbons have derived the relation

$$E_g = E_{CT} - \delta \tag{2}$$

where δ was found to be in the order of 1 eV. For the present investigation, the δ values were calculated and listed in Table 2. It can be seen that there is a close agreement between the δ values for the CT complex of donor (a) with trinitrobenzene (1.05 eV), with those determined by Kuroda. The values for acceptors (3)–(6) are not notably different, while those for the strong acceptors (1) and (2) are quite less, the value being lower as the electron affinity of the acceptor increases, hence causing more π-electron delocalization.

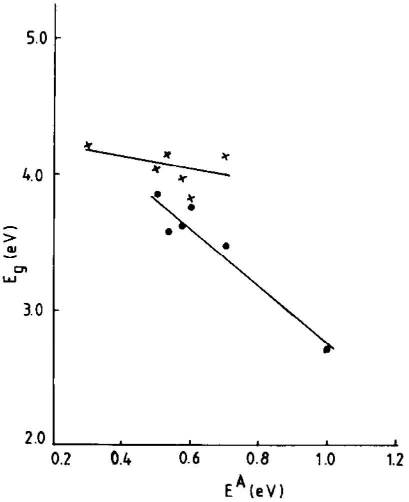

Fig. 5. The variation of energy gaps E_g (eV) as a function of the electron affinity E^A (eV) of the acceptors for 1 : 1 CT complexes of 1,5-diaminonaphthalene (●) and 2,3-diaminonaphthalene (×) with different acceptors.

The conductivity of organic molecular compounds is known to increase with the electron affinity (E^A) of the acceptor [1,12]. Accordingly, the activation energy as well as the energy gaps decrease with increasing conductivity of the compounds. Consequently, a justification for the deduced energy gaps stems from their relation with the electron affinity of the acceptors (the values of E^A are listed in Table 2). Figure 5 shows a plot of the energy gaps of 1 : 1 CT complexes of donors (a) and (b) as a function of the electron affinity for some acceptors. It can be shown that a linear relationship is obtained ($R = 0.95$ and 0.97 for CT complexes of donor (a) and (b), respectively). Therefore it would be reasonable to assume that the conduction process involves excitation of a π-electron from the uppermost filled π-orbital to the lowest empty π-MO [12].

The temperature dependence/electrical conductivity are characterized by two activation energies. This means that the mode of conduction changed during the conductivity measurements. In most cases of CT complexes of donors (a) and (b) of ratio 1 : 1, the activation energy is approximately doubled at higher temperatures; therefore these complexes pass from an externsic regime at low temperatures to an internsic one at higher temperatures [8].

When a potential difference (V) is applied to some CT complexes of donors (a) and (b) of both stoichiometries 1 : 1 and 1 : 2, a current (I) can be measured. Typical characterstic I–V curves are shown in Fig. 6. It can be seen that a straight line relation is obtained, which indicates that the CT complexes have an ohmic character.

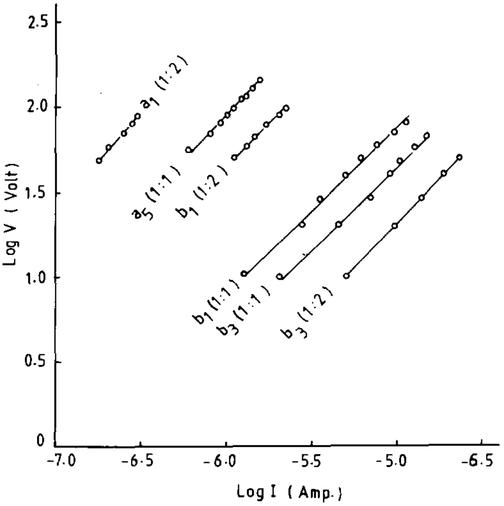

Fig. 6. I–V characteristics obtained for some 1 : 1 and 1 : 2 CT complexes with 1,5-diaminonaphthalene and 2,3-diaminonaphthalene donors.

CONCLUSION

The electrical behaviour of 1 : 1 and 1 : 2 CT complexes is discussed. This indicates that all the CT complexes under consideration display semiconducting behaviour. The activation energy values as well as the energy gaps are quite different for complexes of different stoichiometries obtained from the same donor and acceptor. This can be attributed to the difference in stacking geometry between the donors and the acceptors. The energy gap values for some CT complexes are in agreement with the electron affinity and the excitation charge transfer obtained spectrophotometrically. This is an indication that the conduction process is affected by the electronic excitation from the uppermost occupied molecular orbital to the lowest empty MO.

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