



## Electrical Conductivity of Charge Transfer Complexes of Some Thiophene Schiff Base Complex with Nitrobenzene Acceptors

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The DC electrical conductivity of 2-aminodibenzothiophene added to three different aldehydes which are benzaldehyde, salicylaldehyde and 2,4-dihydroxybenzaldehyde and their charge transfer (CT) complexes with the acceptors, dinitrobenzene (A<sub>1</sub>), 2,4-dinitrophenol (A<sub>2</sub>), picric acid (A<sub>3</sub>) were investigated and have been studied at four different temperatures 20, 30, 40, 50 °C. The rate constant (k) and activation energy of charge transfer compounds were determined using conductivity measurements. It was observed that higher temperatures gradually increase the conductivity and it was lower with increasing molecular weight. Also the increase in the values of conductivity in some compounds was due to the difference in the replacement position of influential groups on the compounds and that of the different electronic resonance. One of the most important study was the general conduct of the donor to acceptor is subject in the form of the first order. We demonstrated that the charge transfer compounds due to the nature of polarity were responsible to a certain extent on the process of conductance. E<sub>a</sub> has been calculated for compounds, it was noted that the discrepancy in values was due to different values of the molecular structure of donors in addition to the different groups replaced them.

**Keywords:** Charge transfer complex, Conductivity, Thiophene-Schiff base, Picric acid, Equilibrium constant.

### INTRODUCTION

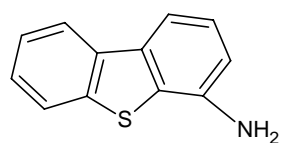
In the last two decades, a vast number of organic compounds have been discovered to exhibit pertinent electrical characteristics<sup>1-4</sup>. Charge transfer complexes are the most important organic species studied because of their special type of interaction, which is accompanied by transfer of an electron from the donor to the acceptor. The temperature dependence of the direct current electrical conductivity of these complexes is usually correlated with the ionization potential of the donor and the electron affinity of the acceptor<sup>4</sup>. Schiff bases are compounds containing an azomethine group known as amines<sup>5</sup>. Schiff bases and their complexes are considered as an important branch in coordination chemistry in current studies proved that are used as antibacterial, antifungal and oxygen carrier properties. The investigations of structure and bonding of Schiff base complexes help to understand the complexes. These structures can be modified through condensation with aldehydes, ketones<sup>6,7</sup>. Schiff base compounds derived from aromatic amines and aromatic aldehydes have a wide range of applications in many fields like biological, inorganic and analytical chemistry<sup>8-12</sup>. They are known to exhibit potent

antibacterial, anticonvulsant and antiinflammatory activities<sup>13</sup>. Schiff bases of isatin derivatives have been used to demonstrate a variety of biological activities, such as antiinflammatory<sup>14</sup> and antidepressant activities. In addition, some Schiff bases show pharmacologically useful activities like anticancer<sup>15</sup>, anti-hypertensive and hypnotic activities<sup>16,17</sup>. Schiff bases are an important class of compounds due to their flexibility, structural similarities with natural biological substances and also due to the presence of imine moiety (-N=CH-) which is potential in elucidating the mechanism of transformation reaction in biological system. These compounds could also act as valuable ligands whose biological activity has been shown to increase on complexation. Because of the fundamental and technological reasons, considerable interest has been shown in the synthesis and study of organic solids and metal complexes which behave like semiconductor materials<sup>18</sup>. The electrical properties of the organic ligands and their complexes have been intensively studied by many of the research groups all over the world<sup>19-26</sup>. Metal complexes of the Schiff bases derived from the reaction of 2-methylbenzopyrrole-3-carboxaldehyde with some aniline derivatives showing slight semiconducting behaviour have been reported<sup>27</sup>. Their conductivity and activation

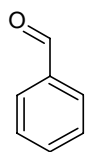
energy were found to depend on molecular structure as well as the ionic radii of the metal ions. The aim of this work is to interpret the structural and conductivity properties of the Schiff base compounds derived from 2-aminodibenzothiophene with benzaldehyde ( $D_1$ ), salicylaldehyde ( $D_2$ ) and 2,4-dihydroxybenzaldehyde ( $D_3$ ). There are many spectroscopic tools utilized to characterize pH complexes, molar conductivity, (NMR, infrared and UV-visible) spectra.

## EXPERIMENTAL

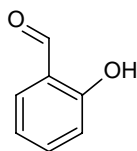
To prepare Schiff bases we used compounds consisting of a primary amine: added 2-aminodibenzothiophene to the three aldehydes are: benzaldehyde, salicylaldehyde and 2,4-dihydroxybenzaldehyde, all from the Laboratory Rasayon (LR).



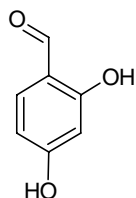
2-Aminodibenzothiophene



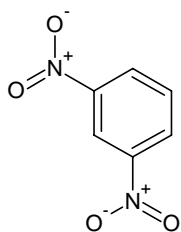
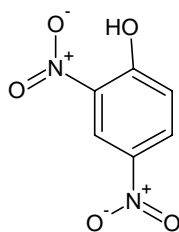
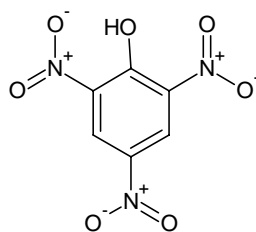
Benzaldehyde



Salicylaldehyde



2,4-Dihydroxybenzaldehyde

1,3-Dinitrobenzene ( $A_1$ )2,4-Dinitrophenol ( $A_2$ )Picric acid ( $A_3$ )

Analysis elements of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) and calculated practical and theoretical percentage and recorded in the Table-1. And comparing these theoretically calculated ratios with those found in practice, was noted that it is close to a large extent. As shown by analysis

of the elemental analysis of the above-mentioned compounds that Schiff bases were obtained with molecular formulas.

Results of elemental analysis, melting points in addition to the molecular formula is clearly points to match the results of the analysis process with the ratios calculated, as can also be charge transfer complexes by 1:1 and 1:2 donors: acceptor.

## MOLECULAR FORMULA OF SCHIFF BASES

Material code	m.f. (m.w.)	Proposed molecular structure
D1	$C_{19}H_{13}NS$ (287.38)	
D2	$C_{19}H_{13}NOS$ (303.38)	
D3	$C_{19}H_{13}NO_2S$ (319.38)	

**Conductivity measurements of the solutions of charge transfer complexes:** Placed 50 mL of the compound of the donor concentration ( $1 \times 10^{-3}$  M) in the flask put it in a water bath at constant temperature. Add acceptor compound prepared at concentration solution ( $1 \times 10^{-4}$  M) at a rate of 0.5 mL every 2 min to the donor compound solution and record reading electrical conductivity. Repeat the previous steps at different temperatures 20, 30, 40, 50 °C and apply to all complex donor and acceptor.

## RESULTS AND DISCUSSION

**Conductivity studies on solution of charge transfer complexes:** The charge transfer (CT) complexes are formed between electron donors, having a sufficiently low ionization potential and acceptors, having sufficiently high electron affinity. The transfer of an electron from a donor to an acceptor is readily possible in the charge transfer process<sup>28</sup>. This work describes connectivity methods which was rapid, simple developed and accurate quantification of Schiff bases in ethanol medium.

**Conductivity measurements of charge transfer complexes:** Conductivity measurements were applied on charge

TABLE-1  
ELEMENTAL ANALYSIS AND MELTING POINT FOR SCHIFF BASE COMPOUNDS AND SOME CHARGE TRANSFER COMPLEXES

Compound	Elemental analysis (%): Calcd. (Found)				Melting point (°C)
	C	H	N	S	
$D_1$	79.41 (79.74)	4.56 (4.55)	4.87 (4.34)	11.16 (11.00)	87-90
$D_1A_3 - 1:1$	58.14 (57.98)	3.12 (3.02)	10.85 (10.39)	6.21 (6.01)	88-91
$D_1A_3 - 1:2$	49.94 (49.74)	2.57 (2.46)	13.15 (12.85)	4.30 (4.03)	75-77
$D_2$	75.22 (75.63)	4.32 (4.47)	4.62 (4.51)	10.57 (10.02)	102-103
$D_2A_3 - 1:1$	56.39 (58.41)	3.03 (3.93)	10.52 (10.25)	6.02 (5.81)	96-98
$D_2A_3 - 1:2$	48.89 (48.69)	2.51 (2.54)	12.87 (12.76)	4.21 (4.20)	102-104
$D_3$	71.45 (70.98)	4.10 (4.18)	4.39 (3.66)	10.04 (10.02)	59-60
$D_3A_3 - 1:1$	54.75 (54.93)	2.94 (2.88)	10.21 (10.76)	5.85 (5.65)	138-140
$D_3A_3 - 1:2$	47.88 (47.92)	2.46 (2.37)	12.61 (12.91)	4.12 (4.06)	54-57

transfer complexes consisting of the compounds donor of electrons and belonging to Schiff bases ( $D_1$ ,  $D_2$ ,  $D_3$ ) receptor and complex belonging to the electrons and nitrobenzene derivatives ( $A_1$ ,  $A_2$ ,  $A_3$ ) at four temperatures (20, 30, 40, 50 °C) and has been raising the concentration of donor compounds ( $1 \times 10^{-3}$  M) ten times the concentration of receptor compounds ( $1 \times 10^{-4}$  M) in order to force the interaction to follow in the direction of the first order. Draw a graph between conductivity at time  $t$  ( $C_t$ ) ( $\mu\text{S}/\text{cm}$ ) versus time (time, min) (Fig. 1) where increasing complex conductivity gradually increase with time until it reaches constant stage connectivity charge transfer complexes. It was affected by two factors, temperature and time, which are important. The values of conductivity were obtained for all charge transfer complexes over the adoption of the values on the nature of the compounds where the receiving picric acid gave the highest values of connectivity with all donor complexes. It was also observed that the conductivity increases with increasing temperature in most cases. This can be explained by the process of electrical conductivity of the solutions of charge transfer complexes that these complexes formed polarizing nature ( $[D] + \delta \cdots [A] - \delta$ ) is working on the passage of electric current through the solution.

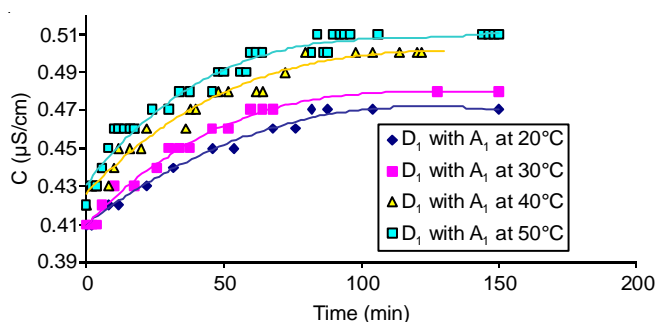


Fig. 1. Relationship between conductivity charge transfer complex ( $\mu\text{S}/\text{cm}$ ) and time (min) of the donor compound  $D_1$  receptors with three different receptors at four different temperatures

The rate of transmission of electrons in complexes with increasing temperature, due to the presence of a larger number of ions in the solution. While indicating low conductivity with increasing temperature to a small number of ions that carry current in the stoichiometry of the overlay. Such behaviour can be interpreted as a rise in temperature with the charge transfer within the molecules overlapped be stronger than the charge transfer between molecules, leading to a shift towards overlapped aggregate form. This is the case in some of the charge transfer complexes<sup>29</sup>.

**Determination of the rate constant (k) of the charge transfer complexes:** The rate of reaction (k) for all donor complexes prepared experimentally with acceptors at four temperatures are determined by applying the following equation:

$$\frac{dC_t}{dt} = k(C_\infty - C_t)^\alpha$$

where  $C_t$  = connectivity at time (t),  $C_\infty$  = connectivity at time ( $t_\infty$ ),  $\alpha$  = the order of reaction,  $\alpha = 1$ .

Taking the logarithm we get the following equation:

$$\ln(C_\infty - C_t) = -kt + \ln C_\infty$$

within the investigated temperature ranges, The plots for  $\ln(C_\infty - C_t)$  versus time (min), observed that the interaction between the donor and acceptor compound is first order (Fig. 2) and the rate constant  $k$  is calculated from the slope. Table-2 illustrates the values of the rate constant for the reaction (k). It is obvious that the temperature increases with continuous increase of the rate constant  $k$  according to the following donor compound  $D_1$  with acceptor compound  $A_1$  of 24.6 to 29.6  $\text{min}^{-1}$  at the temperature change from 20 to 50 °C with the acceptor compound  $A_2$  ranged from 16.7 to 17.7  $\text{min}^{-1}$  and the largest temperature was affected with the acceptor compound  $A_3$  ranged from 22.3 to 48.1  $\text{min}^{-1}$ . In spite of the participation of all donor complex by the presence of the azomethine group ( $-\text{CH}=\text{N}-$ ), but the values of connectivity, as well as the rate constant (k) differs from one donor compound to another with the same acceptor, which refers to the effect of an effective group substituent on the donor and that the effect on the electronic resonance of the molecule and therefore the degree of polarization of the molecule.

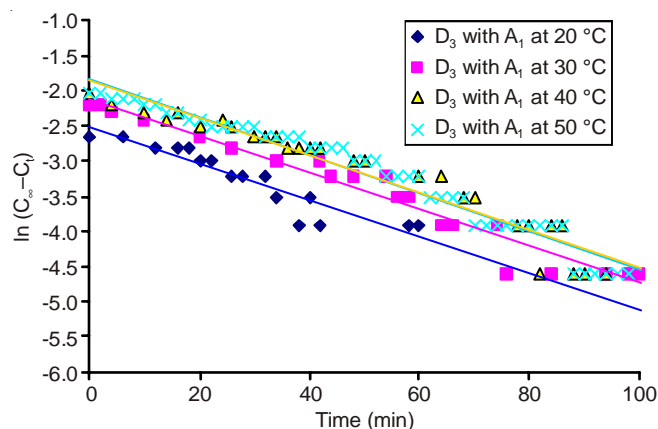


Fig. 2. Relationship between  $\ln(C_\infty - C_t)$  and time (min) of the donor compound  $D_3$  receptors with three different receptors at four different temperatures

The variation of the DC electrical conductivity as a function of the reciprocal of the absolute temperature  $1/T$  for the donor compounds  $D_1$ ,  $D_2$ ,  $D_3$  with the three different acceptors  $A_1$ ,  $A_2$ ,  $A_3$  at four different temperatures are represented in Fig. 3. The curves obtained from the relationship between electrical conductivity and temperature for the charge transfer complexes are represented graphically in Fig. 3. It is obvious that the electrical conductivity increases with the continuous increase of temperature according to the relation<sup>30</sup> by applying the Arrhenius equation:

$$\ln k = \ln A - E_a/RT$$

Since this equation is also obeyed by inorganic semiconductors, it may also be used to describe the electrical properties of organic material (charge transfer complex). The electric conductivity depends largely on the chemical structure of the compounds investigated (Table-2). The values of electrical conductivity of these charge transfer complexes, the activation. Determination of the activation energy ( $E_a$ ) of charge transfer complexes on energy values are given in Table-2. According to the data, the donor compound  $D_1$  with acceptors  $A_1$ ,  $A_2$ ,  $A_3$  ranged between 1.512-18.154  $\text{KJ mol}^{-1} \text{K}^{-1}$ . While the donor

TABLE-2  
VALUES OF EACH OF THE RATE CONSTANT WITH THE FIRST ORDER (k) AND ACTIVATION ENERGY ( $E_a$ ) WITH ACCEPTOR COMPOUNDS ( $A_1, A_2, A_3$ ) OF THE CHARGE TRANSFER USING CONDUCTIVITY MEASUREMENTS

Compound	Temp. (K)	$D_1$		$D_2$		$D_3$	
		$k (\times 10^{-3}, \text{min}^{-1})$	$E_a (\text{KJ mol}^{-1} \text{K}^{-1})$	$k (\times 10^{-3}, \text{min}^{-1})$	$E_a (\text{KJ mol}^{-1} \text{K}^{-1})$	$k (\times 10^{-3}, \text{min}^{-1})$	$E_a (\text{KJ mol}^{-1} \text{K}^{-1})$
$A_1$	293	24.6	3.945	16.2	14.375	25.93	1.156
	303	25.6		17.4		26.2	
	313	24.5		25.8		26.6	
	323	29.6		26.1		27.1	
$A_2$	293	16.7	1.512	24.37	3.773	17.17	18.416
	303	17.1		27.1		18.1	
	313	17.4		27.8		21.4	
	323	17.7		28.3		35.8	
$A_3$	293	22.3	18.154	23.6	1.708	20.69	3.750
	303	28		24.1		22	
	313	28.6		24.6		23.5	
	323	48.1		25.2		23.7	

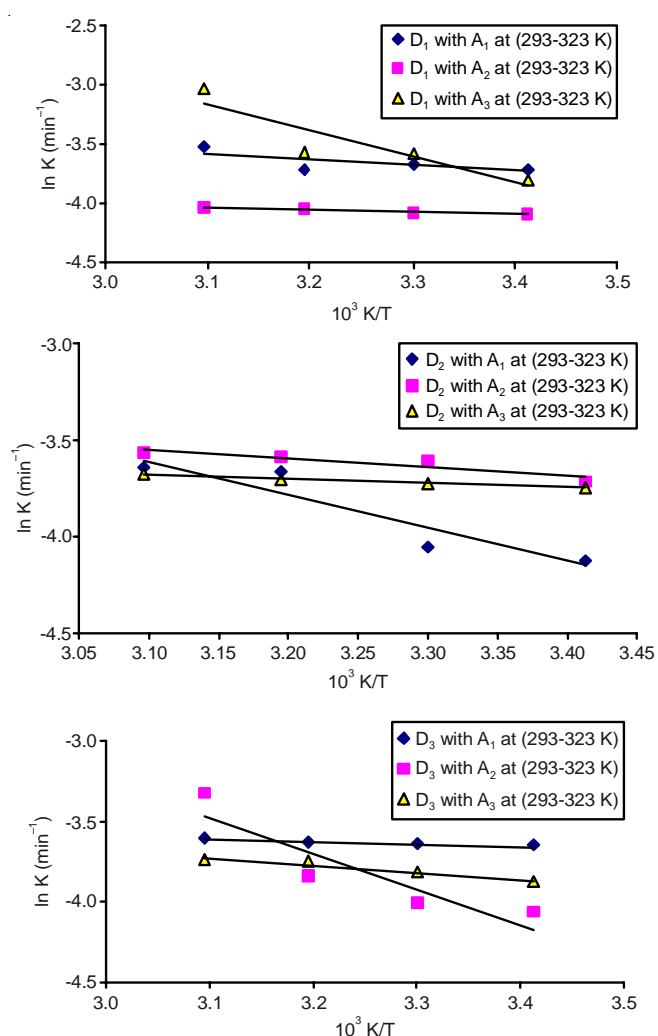


Fig. 3. Linear relationship between  $\ln (K \text{ min}^{-1})$  versus  $1/T$  (K) as an application of the Arrhenius equation for the donor compounds  $D_1, D_2, D_3$ , with three different receptors at four different temperatures

$D_2$  has values between 1.708-14.375  $\text{KJ mol}^{-1} \text{K}^{-1}$  with three acceptors and may be reached and the values of the activation energies of the donor compound  $D_3$  between 1.156-18.416  $\text{KJ mol}^{-1} \text{K}^{-1}$  also with all the acceptors. Comparing the activation energies for charge transfer complexes for donor compound  $D_1$ , we find the following order:

$$D_1A_3 > D_1A_1 > D_1A_2$$

While the donor compound  $D_2$ , we find the following order:

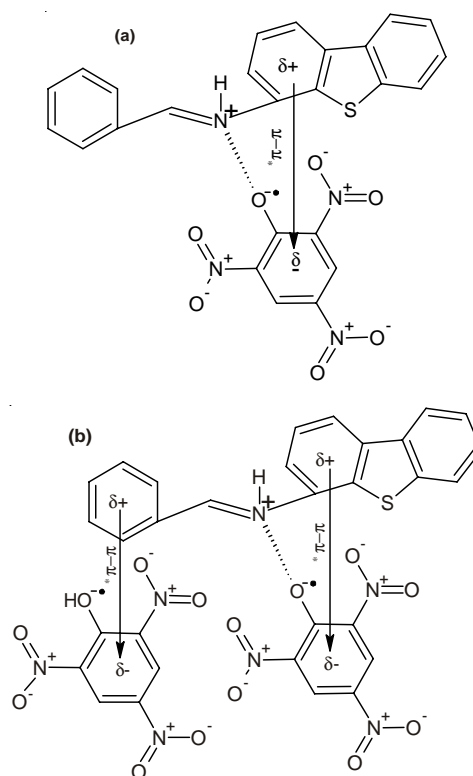
$$D_2A_1 > D_2A_2 > D_2A_3$$

The donor compound  $D_3$ , we find the following order:

$$D_3A_2 > D_3A_3 > D_3A_1$$

The electrical conductivity depends largely on the chemical structure of the compounds investigated. The results may be summarized as follows:

Almost all picric acid complexes exhibit a remarkable increase in electrical conductivity with respect to the corresponding Schiff bases. This can be explained by the fact that picric acid forms complexes through electron transfer from the donor to the acceptor, in addition to proton transfer from the acceptor to the donor.



The molecular structure of overlapping transmission charge resulting from the interaction of the compound with the future  $A_3$  donor compound  $D_1$ : (a) a 1:1 ratio; (b) by 1:2. This configuration indicates, presumably, that the lone pair electrons of the nitrogen atom are no longer capable of contributing to the conduction process.

A remarkable decrease of conductivity is observed in such complexes with increase of temperature. This may be explained by a change in the structure of the charge transfer complex, which may occur through the depolarization of the azomethine  $N^+=H$  group leading to the formation of a weaker complex through  $\pi-\pi^*$  electronic interaction only. The activation energy of 2,4-dinitrophenol complexes is higher than picric acid and 1,3-dinitrobenzene complex.

Complexes of 2,4-dinitrophenol is weaker than the picric acid and 1,3-dinitrobenzene complex, a behaviour which depends on the electron affinities of the acceptors. A behaviour which is due to the participation of both heterocyclic amino and benzyl rings in charge transfer, leading to an increased location of the  $\pi$ -electrons. Consequently, a decrease of electrical conductivity is observed. The dielectric properties of the charge transfer complexes are also studied, it is found that the dielectric ( $\epsilon$ ) increases with temperature.

It is assumed that the higher values of energy of activation are related to the transition of an electron between valence band or localized levels and the conduction band. On the other hand, the smaller activation energies can be due to electron hopping, which is a thermally activated process<sup>31</sup>. A relatively low activation energy is obtained, accompanied by an increase in the conductivity as the temperature increases. This increase could be due to the activation of electrons from the donor level to the conduction band, *i.e.*, extrinsic behaviour. It is interesting to note that the slope of the line, as well as its range of temperature, varies widely depending upon the nature and structure of the complex. The activation energy values of the investigated charge transfer complexes show no correlation with either the electron affinities of the acceptors or the ionization potentials of the donors<sup>32</sup>. This unexpected behaviour indicates that the electronic structure is not the dominating factor in the activation process. The most probable determining factor is the geometrical structure of the complexes. In other words, configurational interactions play a considerable role in the electronic activation process of these species. This is presumably due to the presence of more than one nitro group in the acceptor molecules, in addition to possible orientations of the interacting acceptors and donors in stack arrangements. The configurationally interaction, in a simple form, is electron-phonon interaction. Accordingly, it stimulates some forbidden electronic transition, which may lead to easing of electron migration. In other words, it facilitates the conduction mechanism and hence decreases the activation energies.

The activation energies of the charge transfer complexes are lower than the corresponding values for the donors. The complexation facilitates the mobility of the electrons and, thus, increases the conductivity of the complexes. That means in the charge transfer complexes the energy gap between the valence band (the highest occupied molecular orbital or HOMO, of the donor moiety) and the conduction band (the lowest unoccupied molecular orbital or LUMO, of the acceptor

part) is narrower than that of the HOMO in the valence band and the LUMO in the conduction band of the donor itself. Also, the activation energies of the charge transfer complexes formed by  $\pi-\pi^*$  transitions and resonance stabilization of proton transfer (complexes derived from acidic acceptors) are generally lower than those of the charge transfer complexes derived from 1,3-dinitrobenzene ( $\pi-\pi^*$  transition). The resonance stabilization of the proton transfer causes high stability of the charge transfer complexes and hence the interaction between the molecular orbital's of donor and acceptor increases. This makes both the valence and the conduction bands wider and consequently the energy gap will be smaller.

## Conclusion

Rate constant ( $k$ ) and activation energy of charge transfer compounds were determined using conductivity measurements. It was observed that higher temperatures gradually increase the conductivity and it was lower with increasing molecular weight. Also the increase in the values of conductivity in some compounds was due to the difference in the replacement position of influential groups on the compounds and that of the different electronic resonance. One of the most important that was reached in this study was that the general conduct of the donor with acceptor is subject in the form of the first order. We demonstrated that the charge transfer compounds due to the nature of polarity were responsible to a certain extent on the process of conductance. Activation energy ( $E_a$ ) has been calculated for compounds, it was noted that the discrepancy in values was due to different values of the molecular structure of donors in addition to the different groups replaced them.

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