# Synthesis, Characterization, Thermal and conductivity Study for 1,4-dimethyl-2,5-bis(tellurocyanatomethyl)benzene

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## Abstract

The new Tellurium compound is prepared in two steps. In the first step, p-xylene was reacted with formaldehyde and hydrochloric acid to give 1,4-bis(chloromethyl) -2,5-dimethylbenzene, which was added in the second step to Tellurium powder added to the potassium cyanide compound under an inert atmosphere of argon to give the new compound  and diagnosed by infrared, elemental analysis, visible and ultraviolet rays, mass spectrometry, and nuclear magnetic resonance spectroscopy. At the same time, a thermogravimetric analysis of the compound was carried out to evaluate the thermal stability, and by using the thermal analysis data, the values of the kinetic and thermodynamic functions were extracted, as well as the conductivity at different temperatures was studied.

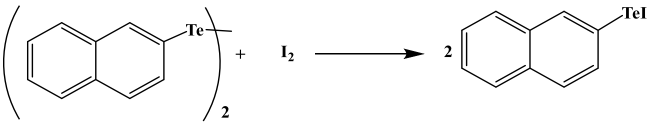
## 1. Introduction

Tellurium was discovery by the scientist Reichenstein in the 1782 year in the minerals located in the “ gold region of Romania ” the scientist Klaproth was able to isolate it from its ores and called it tellurium in relation to the latin word tellus(1-3). Although the compound diethyl telluride is the first organic compound of tellurium that was prepared in 1840 AD by the scientist Fuller Wohler, the real beginning of the preparation of organic tellurium compounds was in the middle of the twentieth century, the reason for the lack of research in previous times is due to the difficulty of preparing Organic tellurium compounds, if their preparation methods require special conditions, being unstable and sensitive to oxygen, light and moisture, as well as their unpleasant smell and high toxicity (4-6) The development of methodology proved the possibility of preparing organic tellurium compounds with high stability by providing the optimal atmosphere and conditions for the preparation reactions represented By using inert gases such as argon gas or high-purity nitrogen as inert atmospheres to expel oxygen and using dry solvents free of moisture and water to prevent the dissolution of these compounds. Research has shown that tellurium compounds derived from organic aromatic compounds are more stable than those derived from aliphatic compounds. (6، 7، 8)

Organic tellurium compounds that contain one tellurium-carbon bond. The tellurium atom in these compounds has double, quadruple or hexavalent valency and can be divided into:

(RTeX) organyltellurenylhalide monoorganic tellurium monohalide

In this type of compounds, only aromatic tellurium compounds of formula 0 can be prepared (I, Br, Cl, F = X : ArTeX). ) )(9-13) Equation 1



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Another tellurium compound diorganyl ditellurium (2-Te-2,Diorganyl ditelluriumR)(14-20) .This type of compound is characterized as solid, orange to red compounds, with the exception of bis(3-chloro-2-pyridyl) ditelluride, which has a mysterious blue colo(21-27). Alkylation of sodium disodium Na2Te2 by two moles of alkyl halide (28,10,9) is one of the most important methods for preparing this type of compound, as in equation 2

$$Na_2Te_2 + 2RX \longrightarrow R_2Te_2 + 2NaX \qquad \text{-------2}$$

In this research prepared and characterization new tellurium compounds dependent of 2,5 bis(chloro methyl) p-xylene to gave and study conductivity , kinetic and thermodynamic parameters.

## 2. *Experiment*

### *2.1 Materials*

P-xylene supplied by Aldrich ,formalin and methanol supplied by UN, hydrochloric acid by Berk, tellurium powder by BDH ,potassium cyanide ,chloroform and anhydrous magnesium sulphate by Merck ,DMSO by HEMEDA ,ether by BDH, ethanol by BWR

### *2.2 Preparation of 2,5 bis(chloromethyl) p-xylene (PPX)*

In a glass flask of 250 ml capacity put 10 gm of p-xylene, 75 ml of formalin solution and 105 ml of concentrated hydrochloric acid. The mixture was left under reflux for five hours. At the end of the reaction, a yellow oily layer was observed on the surface of the reaction mixture. The reaction mixture was cooled and transferred to a glass beaker with a capacity of 500 ml and placed in a cold place for a full day, after which the precipitate layer was isolated and washed several times with methanol to remove acid residues, then left to dry to obtain a white solid with a melting point of 131-132 $^{o}$C with a yield of 70% (29) .

### *2.3 Preparation of 1,4-dimethyl-2,5-bis(tellurocyanatomethyl)benzene*

Pure and dry tellurium powder (4mmole,0.51gm) was added to a dry solution of potassium cyanide (4mmole,0.265gm) in the dry solvent of DMSO (15ml) with continuous stirring for one hour and by the process of reflux in an inert atmosphere of Argon gas and after cooling the mixture to a temperature The laboratory temperature was added to it (0.7gm,4mmole) of the organic compound 2.5 bis(chloro methyl)p-xylene dissolved in 20ml)) of DMSO solvent drop by drop for 15 minutes and then the mixture was stirred for two hours at the laboratory temperature. Then the pale yellow solution was filtered to get rid of the unwanted sediment and the remaining unreacted tellurium element. Then the filtrate was diluted by adding 300 ml of distilled water and the mixture was left for 12 hours. Then it was extracted with ether (15ml × 3) and the organic layer was dried using anhydrous magnesium sulfate. The solution was filtered and then evaporated to give a precipitate that was recrystallized with a mixture of ethyl alcohol and chloroform (2:3) and a crystalline compound was formed and the result was 1.24gm.

## *3.Result and dissection*

### *3.1. FTIR analysis*

The infrared spectra of compound showed the appearance of a strong to medium intensity absorption of two bands of C≡N in the range (2376.38 -2249.07)cm$^{-1}$ (30) . As well as the appearance of two strong to medium intensity absorption bands located (1388.79-1253.77) cm$^{-1}$ attributed to the bending oscillation of the (C-H) aliphatic bond, and at (891.14-802.41)cm$^{-1}$(C-H)aromatic bond. Also, the appearance of a strong intensity beam located at (451.36) cm$^{-1}$, belonging to the Te-C bond, (31)as shown in the Figure(1)

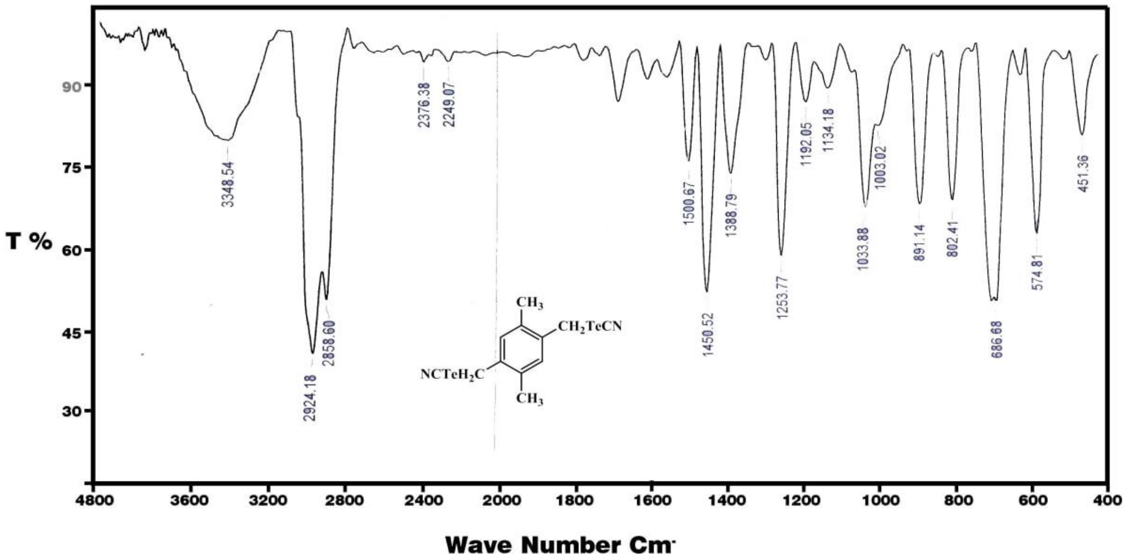


Figure (1) FTIR of1,4-dimethyl-2,5-bis(tellurocyanatomethyl)benzene

### 3.2. CHN Analysis

The practical value of the accurate analysis of the CHN elements for the prepared compound gave a great match with the theoretical value, which confirms the validity of the proposed composition. The practical value of carbon 32.80 while the theoretical value is 31.83 , the practical value of hydrogen 2.75 while the theoretical value is 2.66 and the practical value of nitrogen 6.37 while the theoretical value is 6.23.

### 3.3.Ultra-Vaiolat Analysis

Visible and ultraviolet spectra of all compound prepared in solutions of 1×10-5 M-1×10-4 in DMSO solvent were recorded for a range of wavelengths 200-800 nm. The band that appeared in the range272.5 nm is attributed to the electronic transition (n-π *) caused by the transition of non-bonding electrons from the nitrogen atom to the π * orbitals of the carbon atom. The visible absorption spectra of ultraviolet rays show absorption peaks in the range 256.5nm due to transitions π-π* for the phenyl ring, as shown in the Figure(2).

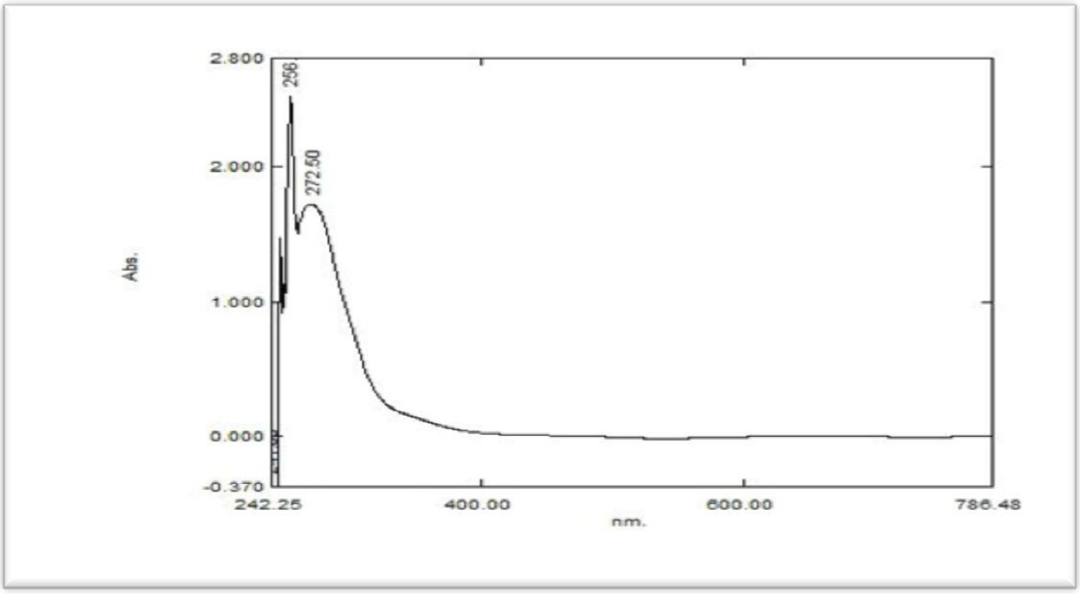


Figure (2) Ultraviolet of ***1,4-dimethyl-2,5-bis(tellurocyanatomethyl)benzene***

### 3.4. Mass spectra

The mass spectrum of the compound shows  bands at 153.2m/z due to the loss of the C11H12TeN ion and the formation of the TeCN ion, the appearance of a basic band at 133.2m/z due to the loss of the Te2CN2 ion and the formation of the C10H12 ion, and the appearance of a band at 106m/z due to the formation of the C8H10 ion. A band appears at 286m/z due to the formation of the C11H12TeN ion as show in Figure (3).

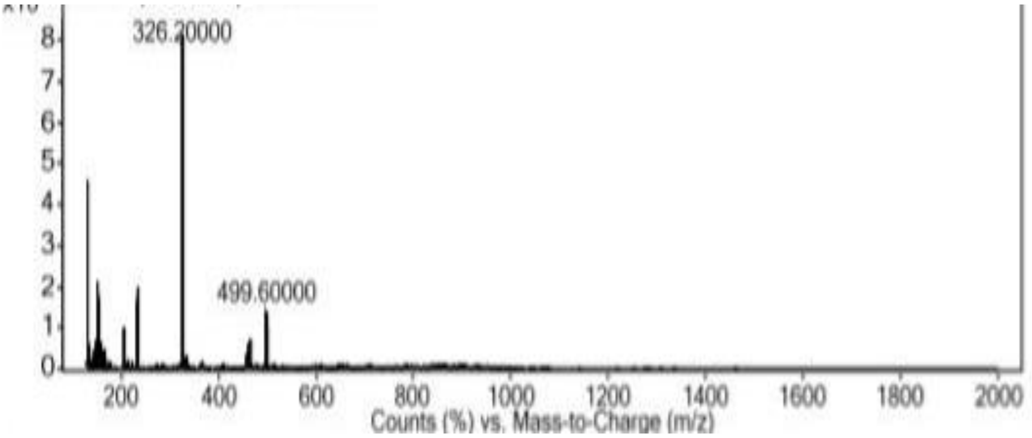
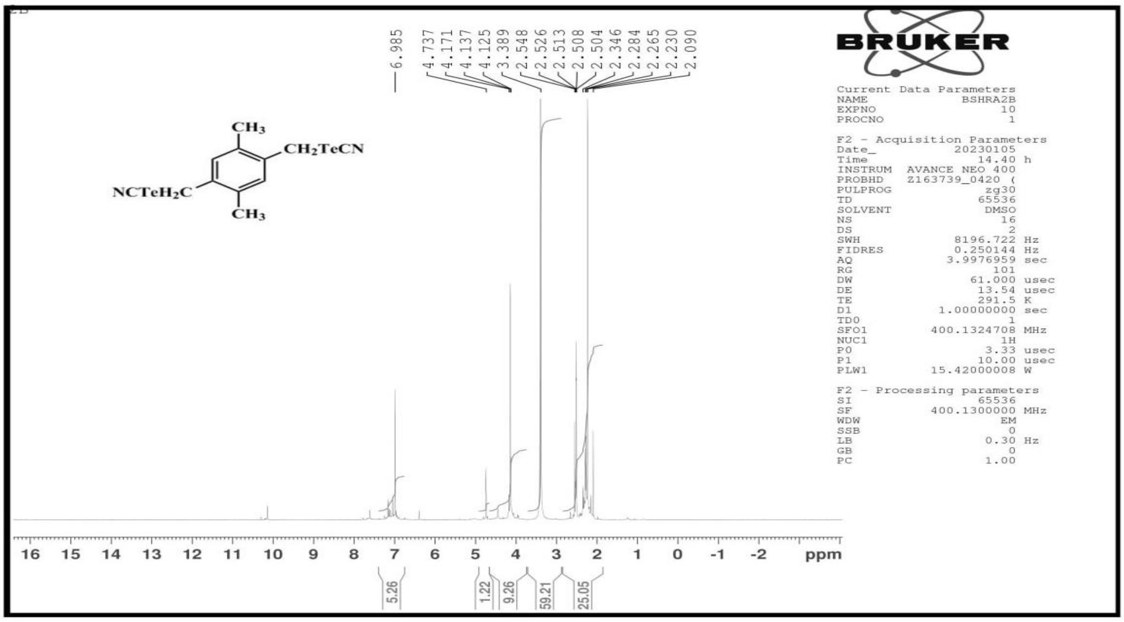


Figure (3) Mass spectra of 1,4-dimethyl-2,5-bis(tellurocyanatomethyl)benzene

## 3.5.H-nmr spectra

The proton NMR spectra were recorded for the compound prepared in DMSO-d6 solvent. And using (TMS) tetramethyl silane as a reference material, as in Figure (4), the chemical displacement values appear for the protons of the vinyl ring, whose spectral signals at the displacement fall in the ppm range (7.00)PPm, Whereas, a spectral signal appears for group $CH_3$ with an offset of (4.30) PPm.for $H_9$,$H_{10}$,and at (2.25)PPm for $H_7$and $H_8$ .



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DE                 13.54 usec
TE                 291.5 K
D1            1.00000000 sec
TD0                    1
SFO1         400.1324708 MHz
NUC1                  1H
P0                  3.33 usec
P1                 10.00 usec
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Figure (4) H-nmr spectra of1,4-dimethyl-2,5-bis(tellurocyanatomethyl)benzene

## 3.5. Thermogravimetric Analysis

Figure (5) show the thermogravimetric analysis of 1,4-dimethyl-2,5-bis(tellurocyanatomethyl)benzene .The data of the phase transitions represented by the dehydration phase, the decomposition phase, and the condensation phase were utilized as specified in the endothermic pyrolysis curve in nature, and this was linked to the thermodynamic coefficients, as the reaction enthalpy ΔH takes positive values This indicates that the reaction is endothermic, as well as the values of ΔG, which have positive values, which indicates that the phase transitions are not spontaneous in nature, calculated using the gravimetric pyrolysis data and considering all phase transitions as first-order reactions. The activation energy and thermodynamic coefficients were determined using the reaction rate equation from first order using Equation 1(32-33):

$$\frac{dx}{dt} = k(1-x) - - - - - - - - - - - - - -1$$

Whereas x

$$x = \frac{w_i - w_t}{w_i - w_f} - - - - - - - - - - - - - - - -2$$

w_i represents the initial weight, w_t is the weight of the model at any point in time t, and w_f represents the final weight of the model(34). Equation (1) can be :rewritten as follows

ln(1-x)=-kt----------------3

Equation 3 was drawn based on the thermogravimetric analysis data as shown in Figure(6) for the prepared compound , and Table (2) show the kinetic and thermodynamic parameters .

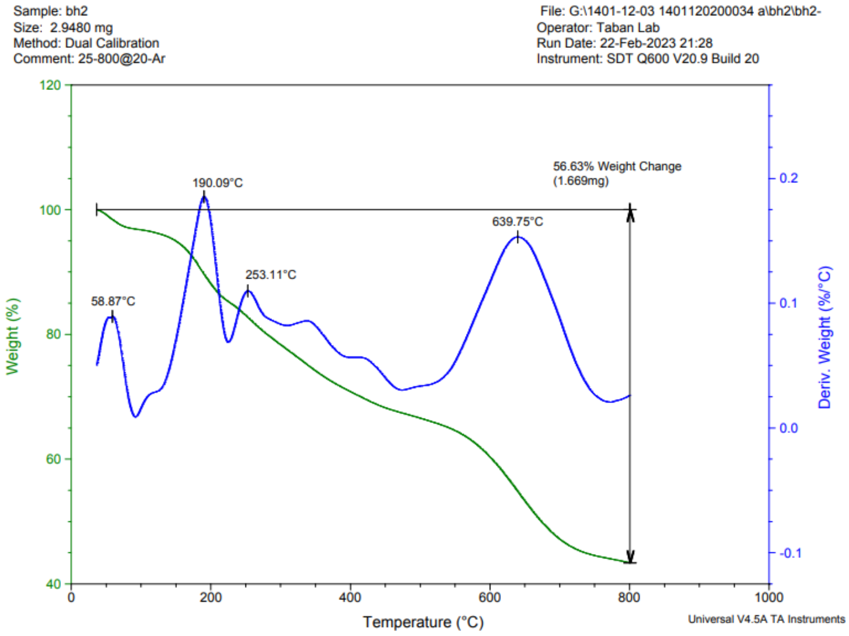

Figure (5) show the thermogravimetric analysis

Table (2) Kinetic and thermodynamic parameters of 1,4-dimethyl-2,5-bis(tellurocyanatomethyl)benzene

| K $min^{-1}$ | $t_{1/2}$ min | Ea $(J.mol^{-1})$ $x10^3$ | ΔH $(J.mol^{-1})$ $x10^3$ | ΔS $(J.mol^{-1}.K^{-1})$ | ΔG $(J.mol^{-1})$ $x10^4$ |
|---|---|---|---|---|---|
| **0.02233** | **31.04** | **13.64585** | **4.7197** | **-1039.6** | **112.0877** |

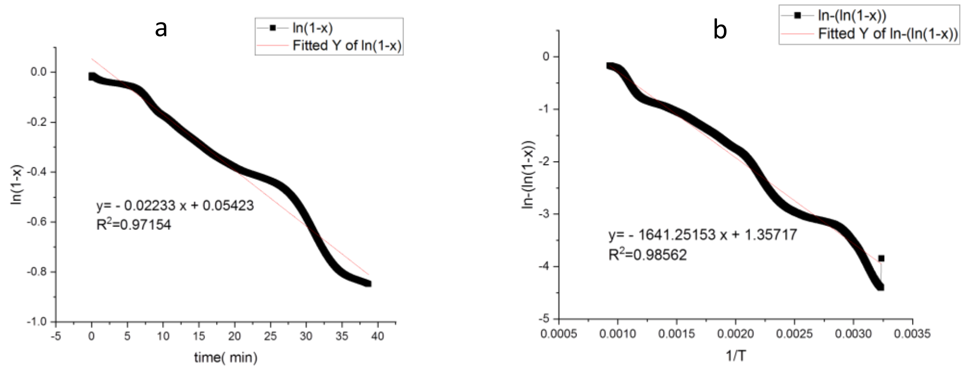

Figure (6) a Plotting the relationship between ln (1-x) against time, b Plotting the relationship between ln [-ln (1-x)] against 1/T

## 3.6.Conductivety study

To measure resistivity value of a layer of an electronic material that is semi-conductor material and metallic material in thin film, four-point prob measure (FPP) is a tool that is commonly used to measure resistivity value is used for this purpose (35).

From current -voltage characteristics of samples by using casting method to preparation it, studied by four probe point measuring technique according to equation 4:

$$\delta_{dc} = \frac{DI}{AV} \text{----------}4$$

Where $\delta_{dc}$resistivity ,D is thickness of film ,I is the current on the circuit ,A is the area of electrode and V is the applied voltage on the film .

Figure (7) show the intrinsic structure -property relationships between current versus voltage that lead to both linear and nonlinear behavior. The ohmic behavior notice at 60 volt at all the sample this can explained by the fact that there negligible injection of charge carriers from outer probes supply current to the sample film because the thermally generated charge carriers are greater than the injected charge from electrodes(36).The deviation from ohmic behavior could be shown at greater voltage than 40 V with another suggested mechanism clarify charge transfer in sample film the same behavior was detected for another system (37) .

In semiconductors the conductivity is thermally activated and typically follows an Arrhenius relationship:

$$\sigma = \sigma_o \; e^{\left(\frac{-E_a}{K_\beta T}\right)} \text{----------}5$$

Where $\sigma_o$ is perfector, $E_a$ is the activation energy $K_\beta$ is the Boltzmann constant and $T$ is the absolute temperature (38) .In Table (3) show decreasing activation energy with increasing temperature and noted ,the sharp increase of conductivity can be attributed to large heat energy absorbed by the sample and thus induced mobility of electrons however the electrical conductivity increases linearly(39) , Figure (8) show Arrhenius relationship.

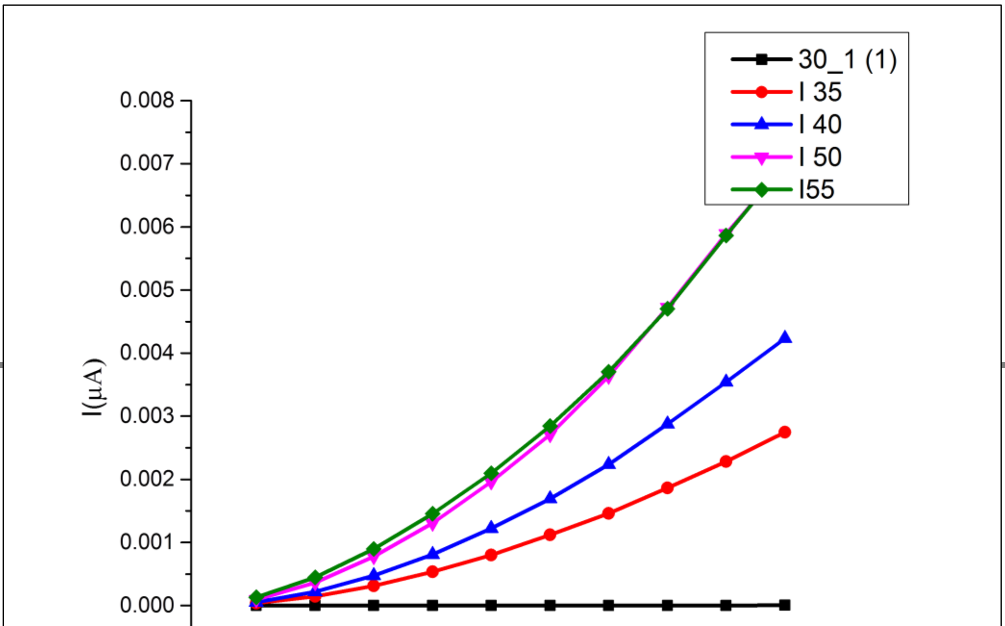

Figure (7) relationships between current versus voltage at different temperatures

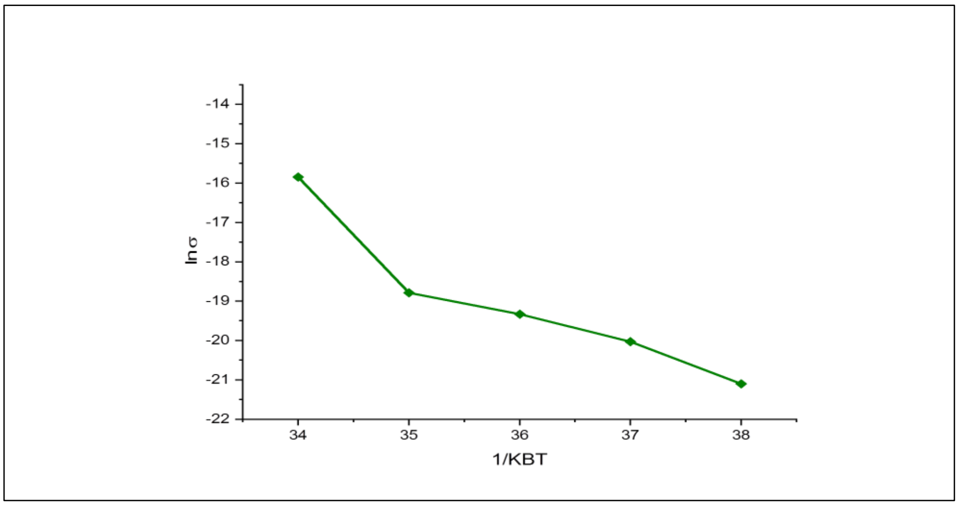

Figure (8) Show Arrhenius relationship

Table (3) Relation  shape between Activation energy and Temperature

| Activation Energy | Temperature |
|---:|---:|
| 6.54E-10 | 303 |
| 2E-9 | 308 |
| 4E-9 | 313 |
| 7.1E-9 | 323 |
| 1.36E-8 | 328 |

## 4.Concolution

The study showed the possibility of preparing aromatic organic compounds with good specifications in electronic transmission processes and could act as semiconductors. The thermal study proved that the compounds have multiple stages of decomposition and are easy to form depending on the relatively low activation energy.

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