

SPECTROSCOPIC AND ELECTRICAL CONDUCTIVITY STUDIES OF SOME SEMICARBAZIDE HYDROCHLORIDE COMPLEXES

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ABSTRACT

The infrared and electronic absorption spectra of semicarbazide hydrochloride and its complexes with anthracene, tetracyanoquinodimethane TCNQ, Na fluorescein and cupferron were recorded in the regions 200-4000 cm^{-1} and 200 - 400 nm. The new bands that appeared in the complex spectra were assigned. The effect of the complex formation on the frequency and intensity of the active vibrational bands was also studied. The internal energy changes of the complexes were calculated in a new line of calculation spectrophotometrically to give a clear insight about the stability of the investigated complexes. The electrical conductivity of the complexes was measured in the temperature range of 25°C to 130°C. The activation energy was calculated and discussed on the basis of the spectroscopic information.

INTRODUCTION

The infrared absorption spectra of semicarbazide hydrochloride (SC. Cl) has been studied by some authors⁽¹⁻⁵⁾ they assigned their different vibrational bands.

Some authors^(6,7) studied the IR spectra of anthracene, naphthalene and naphthacene. They assigned the band at 3050 cm^{-1} to C-H stretching vibration in the anthracene spectra. The other bands at 1625, 1525, 1450, 1325, 1275, 1250, and 1175 cm^{-1} were ascribed to the C-C skeletal vibration of the aromatic ring. The bands at 1000, 950 and 875 cm^{-1} were assigned to different vibrational modes of C-O group. The bands near 725 and 450 cm^{-1} are due to the C-H out of plane deformation vibration.

The UV absorption spectra of semicarbazide hydrochloride (SC. Cl) was recorded by some authors^(8,9). The two absorption bands that appeared at 230 and 260 nm were assigned to the Blue \leftarrow A19 ($\Pi-\Pi^*$) transition. The strong absorption band at 280 nm was assigned to the locally excited ($n\rightarrow\Pi^*$) transition.

Yoshimura et al.⁽¹⁰⁾ studied the UV spectra of NH_4 cupferron and neocupferron. They found that the band at 290 nm of NH_4 cupferron is sensitive to solvents and was considered to be essentially a charge-transfer band.

The electrical conductivity of TCNQ and anthracene charge transfer complexes with pyrene and benzedene was measured^(11,12). They proposed that the conduction is due to hopping mechanism.

The aim of this work is to study the molecular structure of new prepared semicarbazide hydrochloride

complexes with anthracene, cupferron, TCNQ and sodium fluorescein to give clear information about the intermolecular forces and stability of these complexes.

Also, to study the effect of complex formation upon the electrical conductivity and the activation energy of these complexes.

EXPERIMENTAL

The different semicarbazide hydrochloride complexes were prepared by the method described by Melby et al.⁽¹³⁾. The IR spectra were carried out using a Beckman 4250 spectrophotometer. The KBr disc technique was used. The frequencies of the bands are reproducible to within $\pm 1 \text{ cm}^{-1}$.

The electronic spectra of the investigated samples were displayed by Beckman 2560 spectrophotometer. The samples were dissolved in ethanol as a solvent. For the electrical conductivity measurements, the samples were made in the form of discs of 5 mm diameter and 2-3 mm thickness. They were prepared under a pressure of 100 k bar cm^{-2} ($10^5 \text{ bar} = 1 \text{ Pa}$). The surfaces of the samples were covered with a thin graphite layer to achieve good contact. The cell used in the measurements has been described previously⁽¹⁴⁾. The temperature was measured by a copper constantan thermocouple placed close to the sample. The direct current was measured by a Keithley Electrometer type 610B.

RESULTS AND DISCUSSION

The IR absorption spectra of SC. Cl and its complexes with anthracene, TCNQ, cupferron and sodium fluorescein are recorded and shown in Fig. (1). The different IR absorption bands in each case and their

Table (1) : The IR spectra of Sc. Cl and its complexes in the 2000-200 cm^{-1} region.

Sc. Cl	Cupferron Sc. Cl	Anthracene Sc. Cl	Na Fluorescein Sc. Cl	TCNQ Sc. Cl	Assignment
		3800 m	3500 m		$\nu(\text{OH})$
3400 m	3400 m	3400 m	3400 m	3400	$\nu_{\text{as}}(\text{NH}_2)$
3250 m	3250 m	3250 m	3250 m	3200 m	$\nu_{\text{s}}(\text{NH}_2)$
	3150 m		3050 m	3050 m	$\nu(\text{NH})$
2800 m	2850 m	2900 m	2925 m	2900 m	$\nu_{\text{as}}(\text{NH}_3)$
2600 m	2625 m	2650 m	2700 m	2675 m	$\nu_{\text{s}}(\text{NH}_3)$
2300 m	2350 m	2350 m	2350 m	2300 m	$\text{NH}^+ \text{Cl}^-$
				2200 v.s	C N
			1700 m	1760 m	C=N
1675 m	1675 m	1675 m		1675 m	$\nu(\text{C=O}), \nu(\text{CN}) \& \delta \text{NCN}$
1550 m		1550 m	1575 s	1525 m	$\delta(\text{NH}) \& \nu(\text{CN})$
1525 w		1450 m	1450 m		$\delta_{\text{s}}(\text{NH}_3)$
1475 m					
1375 m	1375 s	1375 m	1375 m	1350 m	$\delta(\text{NH}), \nu(\text{CN})$
	1325 sh				N-N str. vib.
	1300 m				Ring Vib.
	1275 m		1275 m		
	1200 m	1200 w	1200 m	1200 m	r (NN)
1175 m	1175 m	1175 m	1175 m	1175 sh	r (NH ₂)
1125 sh	1125 sh	1125 sh	1125 m	1125 sh	r (NH)
	1100 v				$\delta(\text{OH})$
1050 sh		1075 sh	1025 m	1025 m	r (NH ₃)
925 m	925 s	925 s	900 m	925 s	r (NH ₃), $\nu(\text{CN})$
		875 m	875 s	875 vs	$\nu(\text{CN}), r(\text{NH}_3)$
750 m	750 m	750 m	750 m	750 m	$\tau(\text{NH}_2)$
700 v					
	675 m		650 m		C (CN)
500 m		500 s			$\delta(\text{NCN})$
	475 m		450 m	450 m	

v stretching

v strong

 δ bending

w wagging

m medium

 τ torsion

sh shoulder

as asymmetric

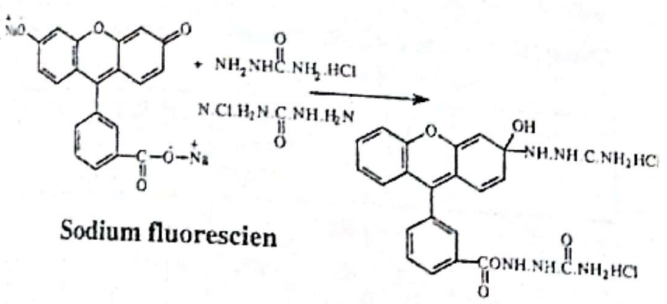
r rocking

vs very strong

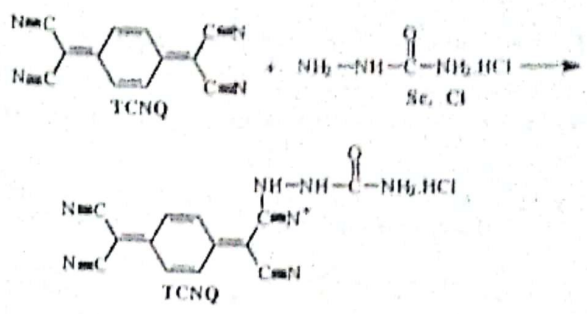
s symmetric

assignments are tabulated in Table (1). Comparison between the IR spectra of the investigated complexes and the parent compound show that new bands appeared as a result of the complex formation. Also, some bands show detectable frequency and intensity changes.

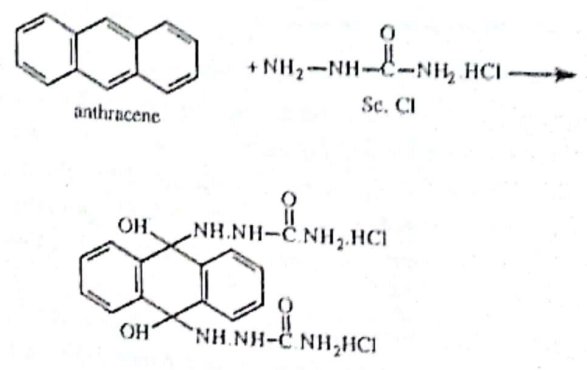
For sodium fluorescein SC. Cl complex, the new band at 650 cm^{-1} can be attributed to the inactive transitional bending vibration of the C-N group resulting from the interaction of the Sc. Cl molecule with the sodium fluorescein. Also, another new band appeared at 1275 cm^{-1} which may be due to the -C=ONa of the sodium fluorescein molecule. The condensation of the sodium carboxylic group of sodium fluorescein with a SC. Cl molecule lead to the removal of H_2O molecule forming the -C=O group. The carbonyl band at 1675 cm^{-1} in Sc. Cl spectra is shifted to 1700 cm^{-1} in the spectra of the complex. This shift is due to the addition reaction between the amino group of Sc. Cl with the carbonyl group of sodium fluorescein. The frequency shift of the 1550 cm^{-1} band in the IR spectra of Sc. Cl to 1575 cm^{-1} in the spectra of the complex may be due to the coupling of the C-C ring stretching vibration of the sodium fluorescein molecule with the C-n stretching vibration of the SC. Cl molecule. The proposed molecular structure is as follows:



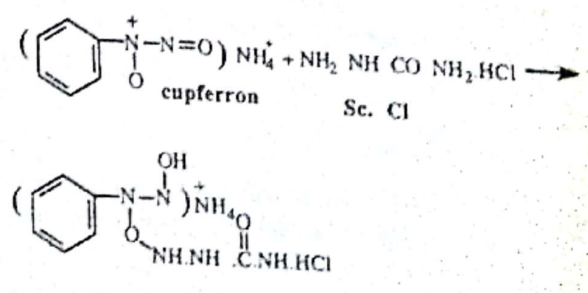
The infrared spectra of TCNQ-Sc. Cl shows a strong new absorption band at 1760 cm^{-1} . This band is due to the C=N stretching vibration. The appearance of this band indicates that the interaction takes place through the nitrogen atom of one of the active cyano group of TCNQ molecule forming a C=N group during the complex formation. This can be supported by the appearance of C≡N stretching vibration at 2200 cm^{-1} which is the range of bonded CN stretching vibration⁽⁹⁾. A new band also appeared as 3050 cm^{-1} in the spectra of TCNQ-Sc. Cl complex which is due to the transformation of NH_2 group of Sc. Cl to NH group by a complex formation. This finding supports the proposed structure of TCNQ-Sc. Cl complex in which the complex is formed through the electrophilic addition of the amino group of Sc. Cl to the one cyano group of TCNQ as follows:



The IR absorption spectra of anthracene-Sc. Cl complex show a new band appearing at 3800 cm^{-1} which is due to the OH stretching vibration. The appearance of this band in the complex spectra indicates the hydrolysis of anthracene Sc. Cl complex during the reaction with Sc. Cl molecules forming the hydroxyl group.



The IR spectra of the Sc. Cl cupferron complex shows a new band at 1100 cm^{-1} , Fig. (1). This band is due to the bending OH vibration. The absorption band observed at 3150 cm^{-1} in the spectra of cupferron Sc. Cl is attributed to the N-H stretching vibration formed as a result of complex formation. This is aided by the disappearance of the NH_2 band at 1550 cm^{-1} in the IR spectra of Sc. Cl. The proposed molecular structure of cupferron Sc. Cl complex is as follows:



From Table (1) it is observed that the vibrational bands at 2800 and 2600 cm^{-1} of the NH_3 stretching vibration show a detectable frequency shift in the spectra of all Sc. Cl complexes. This shift is in the following order: cupferron Sc. Cl < anthracene Sc. Cl < TCNQ-Sc. Cl < Na fluorescein Sc. Cl. This order gives qualitative analysis about the extent of interaction

and reflects the stability order of these complexes.

The absorbance of the infrared bands with relevant intensity for Sc. Cl and its complexes are shown in Table (2).

Table (2). The integrated intensity ($A \times 10^{-4}$) of the absorption bands with relevant intensity of the Sc. Cl complexes.

Wave No. (cm^{-1})	Sc.Cl	Cup-Sc. Cl	Anth-Sc. Cl	TCNQ-Sc. Cl	Na-Flour-Sc. Cl	Assign-ment
2800	1.3	1.8	2.2	2.6	3.2	NH_3
2600	1.8	3.2	3.5	3.8	4.0	NH_3
2300	0.4	2.1	2.2	2.7	2.7	NH^+Cl^-
1675	5.1	5.6	6.6	7.1	7.6	C=O
700	3.2	4.1	4.6	4.6	4.6	NH_2

This table reflects the following order for the stability of these complexes: cupferron Sc. Cl < anthracene Sc. Cl < TCNQ-Sc. Cl < sodium fluorescein Sc. Cl. This order is in parallel with the order obtained from the frequency shift and gives qualitative information about the stability of the investigated complexes.

To give a quantitative study of the stability of these complexes, the internal energy is calculated differently. It is calculated, spectrophotometrically, by calculating the vibrational and rotational energies from Plank's energy relation $E=h\nu$.

The energy changes are connected with the stability of the complexes. The rotational and vibrational energies of the ligand (Sc. Cl) can be given by:

$$E_L = N h C \nu = N h C \sum (\nu_1 + \nu_2 + \dots + \nu_n)$$

Where N is Avogadro's number, h is plank's constant, C is the velocity of light and ν is the summation of wave numbers $\nu_1, \nu_2, \dots, \nu_n$ occurring in the infrared spectra of the different complexes.

The difference in the energy of Sc. Cl and its complexes is given by:

$$\delta E = E_L - E_C = N h C \sum \delta \nu$$

Where $\delta \nu$ is the difference in wave numbers of the ligand and its complexes. δE is a quantitative value for the stability of the formed complexes and also represents the charge transfer energy involved in the complex formation.

The values of the internal energy of Sc. Cl and its complexes are listed in Table (3). The plots of frequency or intensity changes of the NH_3 vibration against the internal energy, Figs. (2 & 3), for the different Sc. Cl complexes are good linear relationships obeying the following empirical formulae:

$$\delta E = 0.03 A + 2.94 \text{ and } \delta E = 0.001 \nu + 0.004$$

Table (3): The vibrational rotational energy for Sc. Cl and its complexes.

Sample	$\sum \nu \text{ cm}^{-1}$	E (KCal/mol)
Sc. Cl	29700	84.73
Cupferron-Sc. Cl	28775	80.08
Anth-Sc. Cl	30825	88.84
TCNQ-Sc. Cl	34625	98.08
Na-Fluorescein-Sc. Cl	39475	104.06

The electronic absorption spectra of semicarbazide hydrochloride and its complexes have been recorded in the range 200 - 400 nm, Fig. (4). Three absorption bands appeared in the spectra of Sc. Cl at 230, 260 and 280 nm. The shorter wavelength bands at 230 and 260 nm can be assigned to $\Pi \rightarrow \Pi^*$ and the longer wavelength band at 280 nm can be assigned to $n \rightarrow \Pi$ locally excited transition.

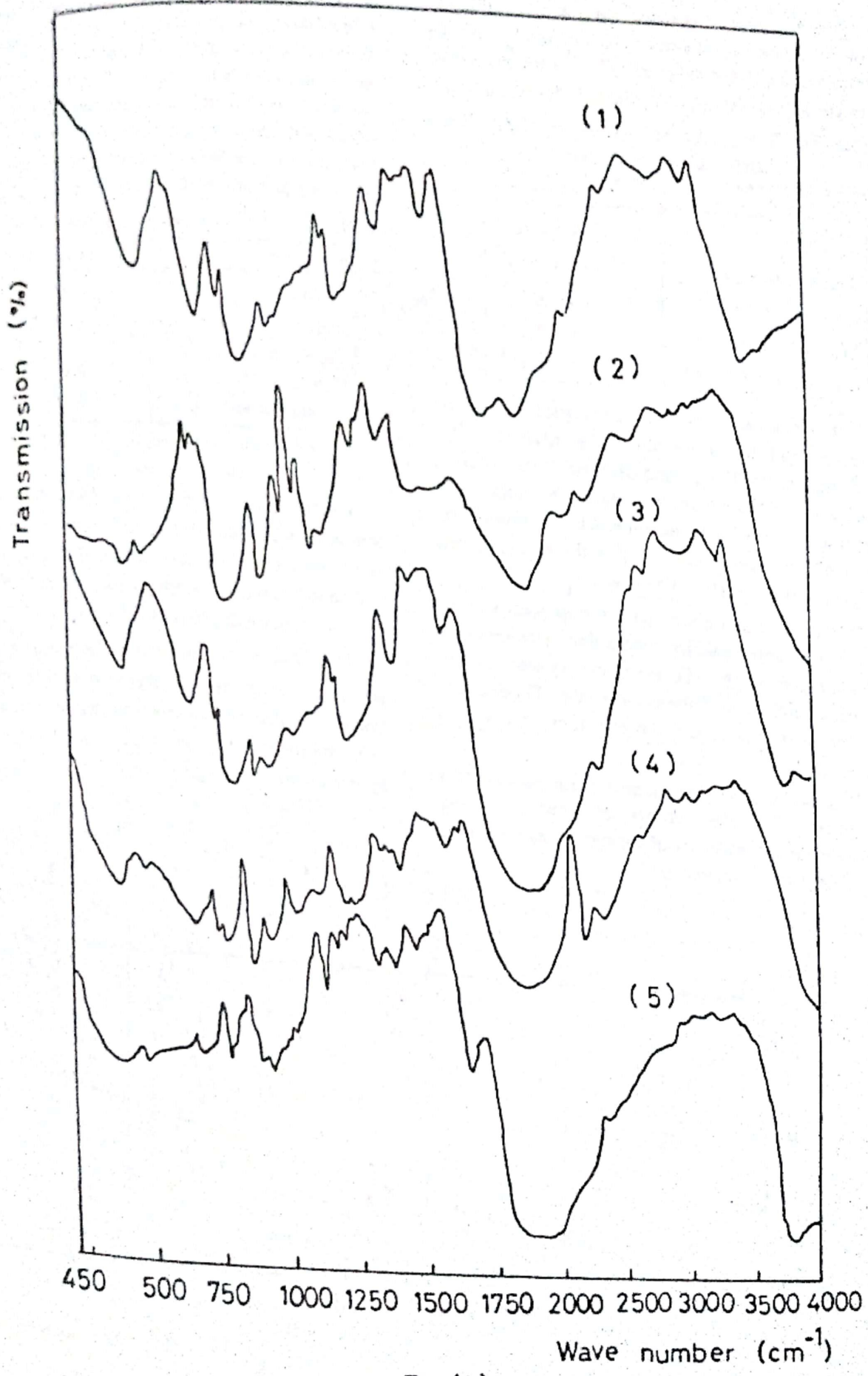
The characteristic features of the spectra are given in Table (4). Comparing the spectra of Sc. Cl with that of its complexes, it is clear to observe that the broad band at 230 nm is shifted to $210 \pm \text{nm}$ in all the complexes. Also, the spectra of the complexes show a maximum absorption band at 260 nm overlapped with the weak band at 280 nm.

Table (4): The electronic absorption bands and their intensities of Sc. Cl and their complexes in ethanol solution.

Compound	λ_{max} (nm)	$\epsilon \times 10^{-3}$	λ_{max} (nm)	$\epsilon \times 10^{-3}$	λ_{max} (nm)	$\epsilon \times 10^{-3}$
	$\Pi-\Pi^*$		$\Pi-\Pi^*$		$n-\Pi^*$	
Sc. Cl	230	80	260	38	280	5
Anth-Sc. Cl	212	90	260	40	-	-
TCNQ-Sc. Cl	210	120	260	50	-	-
Cupferron-Sc. Cl	212	80	260	35	-	-
Na-fluorescein-	211	140	260	100	-	-

The calculated intensity of the locally excited bands (ϵ) are given in Table (4). From this table it is clear to observe that the intensity of the locally excited band at 260 nm of the complexes is higher than that of the parent compound. This relative increase in the intensity of the locally excited bands indicates the presence of $\Pi \leftarrow \Pi^*$ charge transfer interaction between the interacted molecules in addition to the interaction between the active side groups. This type of interaction increases the delocalization of the Π -electronic system on the molecule and subsequently increases the probability of the transition, i.e. increases the intensity of the transition.

The electrical resistivities (ρ) of the investigated



Fig(1)

compounds room temperature are given in Table (5). From this table, the electrical resistivities of the complexes are in lite range of 10^8 - 10^9 ohm. cm. which correspond with the typical semiconductor resistivites.

Table (5): The electrical resistivities (ρ) of Sc. Cl and its complexes at room temperature (25°C),

Substance	π (ohm. cm)
Sc. Cl	4.1×10^{10}
Anthracene Sc. Cl	4.4×10^8
Cupferron Sc. Cl	6.3×10^8
TCNQ-Sc. Cl	1.4×10^9
Na fluorescein-Sc. Cl	5.0×10^9

The electrical resistivities of cupferron, sodium fluoresceinand anthracene are in the range of 10^{11} - 10^{13} ohm.cm⁽¹⁵⁾. The general decrease in the electrical resistivities of hte studied complexes than that of the parent compound can be interpreted by considering hte effect of complex formation upon the electronic and molecular structure of Sc. Cl molecule.

The infrared and electronic spectroscopies indicate that the charge transfer interaction increases the delocalization of the Π electronic system on the complex molecule. Subsequently the Π electrons become more mobile and the excitation energy then decreases.

This mechanism permits a great participation of the Π electrons in the process of conduction and consequently the resistivity of the complexes is less than that of the parent compound.

The electrical resistivity was measured in the temperature range 25-130°C. The temperature dependence of the electrical resistivity of Sc. Cl and its complexes is shown in Fig. (5). The linear increase of $\log \rho$ with $1/T$ indicates that these materials behave like typical intrinsic semiconductor materials. The activation energies (E) have been calculated from the slope of the linear relations of Fig. (5) and are given in Table (6).

Table (6): Activation energies of the studied complexes.

Substance	π (ohm. cm)
Sc. Cl	0.97
Anthracene Sc. Cl	0.58
Cupferron Sc. Cl	0.61
TCNQ-Sc. Cl	0.57
Na fluorescein-Sc. Cl	0.54

From this table it can be observed that the activation energies of the complexes are about $(0.58 \pm 0.03$ ev). This value is less than that of Sc. Cl by (0.4 ev). This decrease in the activation energy is equivalent to the energy change of U.V. spectral line at 230 nm which is shifted to 212 nm by complex formation. This frequency shift is corresponding to 0.45 e.v.

Also, this table shows that the sequence of the activation energy is in accordance with the stability order evaluated from the spectroscopic studies. This confirme the contribution of the interacted Π - electron system on hte conduction process.

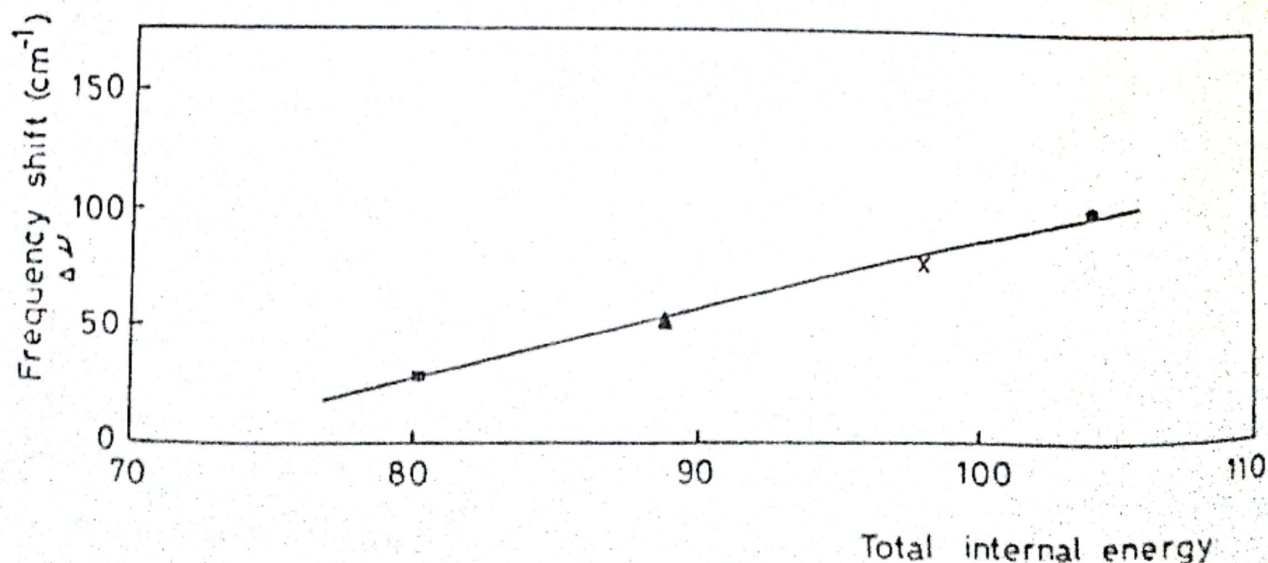


Fig. (2)

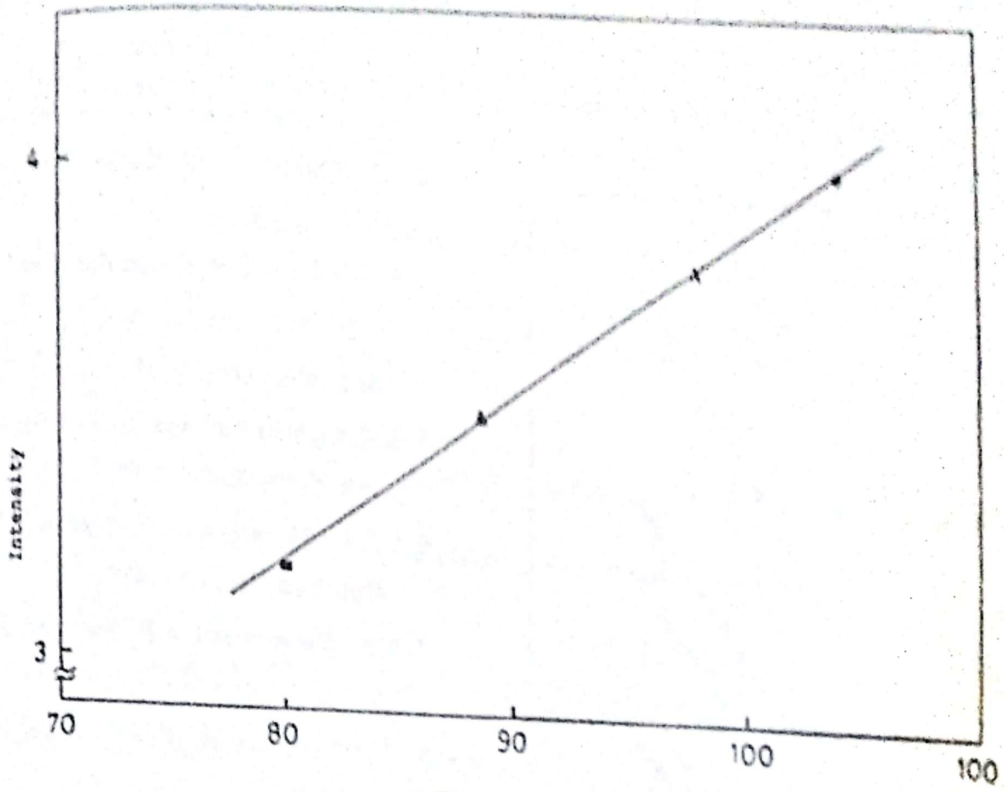


Fig. (3a) Total internal energy

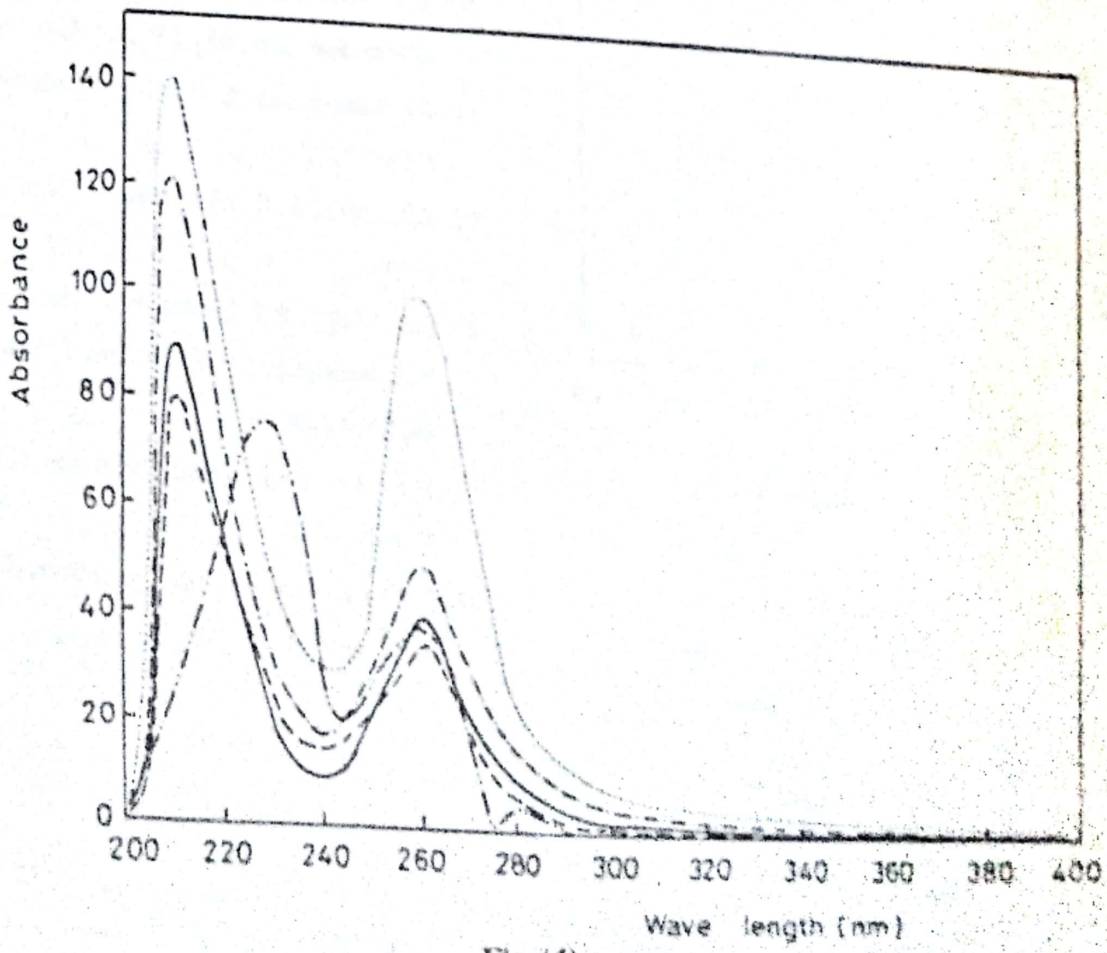


Fig. (4)

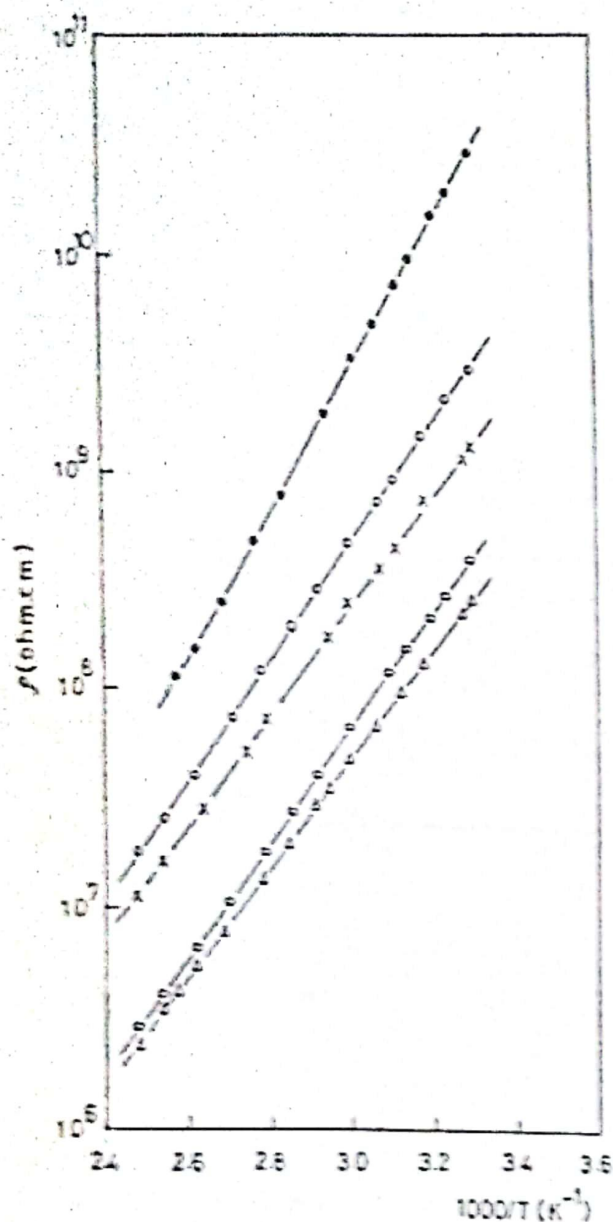


Fig. (5)

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دراسات طيفية وكهربية لبعض مركبات السيميكاربازيد هيدروكلوريد

ممدوح عاكف فضلى و ماجدة ضوى بدرى*

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تم قياس طيف الأشعة تحت الحمراء والطيف الالكترونى لسيميكاربازيد هيدروكلوريد ومركباته مع الانثراسين ورباعى كينوثنائى الميثن وفلوروسين الصوديوم والكافرون فى المدى من ٢٠٠-٤٠٠٠ سم^{-١}، ٢٠٠-٤٠٠ نانوميتر.

وقد تم دراسة تأثير تكوين تلك المركبات على تردد وشدة أشرطة امتصاص هذه المركبات. ولالقاء الضوء على مدى ثبات هذه المركبات فقد تم حساب الطاقة الداخلية لهذه المركبات بطريقة طيفية. وقد تم أيضا دراسة خواص التوصيل الكهبرى لهذه المركبات فى مدى درجات الحرارة من ٢٥-١٣٠°م وقد تم حساب طاقة التمشيط لهذه المركبات ومناقشتها فى ضوء المعلومات الطيفية.