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SPECTROSCOPIC AND THERMAL STUDIES ON CHARGE-TRANSFER COMPLEXES OF THIOMORPHOLINE WITH P-CHLORANIL,2,3-DICHLORO-5,6-DICYANO-1,4-BENZO QUINONE AND 7, 7′,8,8′-TETRACYANOQUINODIMETHANE

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ABSTRACT

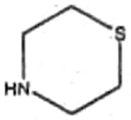
The electron donor/acceptor interactions of thiomorpholine (TM) with DDQ, CHL and TCNQ in chloroform as solvent have been produced stable complexes with general formula [(TM)(acceptor)] with molar ratio 1:1 acceptor: donor. The elemental analysis (CHN), electronic spectra, photometric titration, infrared spectra as well as thermogravimetric analysis (TGA/DTG) were used to give known idea about the charge-transfer interaction between donating and accepting sites. Benesi-Hildebrand and its modification methods were applied to determination of association constant (K), molar absorbtivity (ε).

INTRODUCTION

Many of the electron donor-acceptor (EDA) interactions had been widely studied spectrophotometrically in the determination of drugs that are easy to be determined based on CT- complex formation with some electron acceptors (1-3).

The study of the charge-transfer complexes formed in the reaction of aromatic electron acceptors (π-acceptors) with various electron donors have attracted considerable interests and growing importance owing to their significant physical and chemical properties (4, 5). A vast number of the charge-transfer complexes formed during the reaction of σ- and π-acceptors with organic compounds containing different sites of donation (nitrogen, oxygen or sulfur atoms) were extensively investigated (6-10). This paper is a continuation of our previous investigation(11-14) concerned with the formation of stable charge-transfer complexes formed during the reaction of electron donors.

The present investigation tends to elucidate mainly the study of the reactions of *p*-chloranil (CHL), 2,3-dichloro-5,6-dicyano-1,4- benzo quinone (DDQ) and 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) (π-acceptors) for the first time with thiomorpholine (TM, Formula 1) (electron donors) and interpreting the nature of these interactions using elemental analysis data (CHN), infrared spectra, electronic absorption as well as thermogravimetric analysis.



Formula 1: Thiomorpholine (TM)

EXPERIMENTAL

Reagent grade chemicals were used without further purification. Thiomorpholine was obtained from Aldrich Chemical Co. while *p*-chloranil (CHL), 2,3-dichloro-5,6-dicyano-1,4- benzoquinone (DDQ) and 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) were obtained from Merck Chemical Co.

Analysis and physical measurements

Microanalysis for carbon, hydrogen, nitrogen and chloride were carried out at the Micro analytical centers, Cairo University, Cairo, Egypt using a Perkin Elmer CHN 2400. Electronic spectra were recorded at room temperature via Jenway 6405 Spectrophotometer. IR-spectra, as KBr discs, were recorded on a Bruker FT-IR spectrophotometer (400-4000 cm^{-1}). The thermal analysis (TGA & DTG) was carried under nitrogen atmosphere with a heating rate of 10 C/min using a Shimadzu TGA-50H thermal analyzers.

Photometric measurements

The photometric titration measurements were carried out within the reactions between the acceptors, (CHL, DDQ and TCNQ) and the donor (thiomorpholine, TM) in $CHCl_3$ at 25 °C. The concentration of the donor in the reaction mixtures was kept fixed at (1.0×10^{-4} M) while the concentration of the π-acceptors (CHL, DDQ and TCNQ) changed over a wide range of concentrations (0.25×10^{-4} M to 3.0×10^{-4}

M) to produce solution in each case of (donor: acceptor) molar ratio varying from (1.0: 0.25) to (1.0: 3.0). The peak absorbance of the resulted CT-complexes at 403 and 555 nm for [(TM)(DDQ)], 292 and 552 nm for [(TM)(CHL)], and (329 and 562 nm) for [(TM)(TCNQ)] were measured for each reaction mixture and plotted as a function of the three acceptors (CHL, DDQ or TCNQ) to TM donor molar ratio. The stoichiometry of the molecular CT- complexes under investigation were determined by the application of the conventional spectrophotometric molar ratio according to the known methods (15) and were also used to obtain the modified Benesi-Hildebrand plots(16-18) in order to calculate the formation constant, K, and the molar absorbtivity, ε, values for each CT- complexes resulted from this study.

Preparation and characterization of the CT-complexes

The solid CT complex of (TM) with acceptors (CHL, DDQ and TCNQ) were prepared by mixing 1 mmol of the donor in chloroform (10 mL) with 1 mmol of the each acceptors in the same solvent with constant stirring for about 20 min. The solutions were allowed to evaporate slowly at room temperature over night, the solids filtered and washed several times with little amounts of solvent, and dried under vacuum over anhydrous calcium chloride. The charge-transfer complexes [(TM)(DDQ)] (brown) formed with empirical formula as $C_{12}H_9N_3SCl_2O_2$ with molecular weight 330 g/mol, [(TM)(CHL)] (brown) formed with empirical formula as $C_{16}H_9NCl_4SO_2$ with molecular weight 349 g/mol and [(TM)(TCNQ)] (green) formed with empirical formula as $C_{19}H_{22}N_4S$ with molecular weight 338 g/mol.

RESULTS AND DISCUSSION

The elemental analysis data (CHN) of the TM charge transfer complexes were performances and listed in Table 1. From this Table, it can see that the resulted values are agree quite well with the calculated values, and the suggested of the CT-complexes is matched with the molar ratios introduced from the photometric titration curves.

Electronic spectra

The electronic absorption spectra of the reaction mixtures containing CHL, DDQ and TCNQ with TM as donor in $CHCl_3$ show absorption bands located at (292 and 552 nm) for TM/CHL, at (403 and 555 nm) for TM/DDQ and at 329 and 562 nm for TM/TCNQ (Fig. 1A, B and C). These detected absorption bands do not belong to any of the reactants and well known to be characteristic of the formation of new CT-complexes; [(TM)(CHL)], [(TM)(DDQ)] and [(TM)(TCNQ)]. The stoichiometry of the CT complexes was determined by applying known method(15). Photometric titrations between (TM) and respective π-acceptors reveal that the stoichiometry of the reaction mixtures is 1:1 (Fig. 2A, B and C). This criteria was agree quite well with the elemental analysis data obtained from the isolated solid CT-complexes as presented in the Table 1, as well as from the complexes infrared spectra, which indicate the existence of the bands characteristic for both the TM and the acceptors.

The formation constant (K) values and molar absorbtivity (ε) of the CT complexes studies have been determined using the 1:1 modified Benesi-Hildebrand equation (1)(17). C_a^o and C_d^o are the initial concentrations of the represented acceptors (CHL, DDQ and TCNQ) and the donor TM, respectively, while A is the absorbance of the CT-complexation bands around 552 nm for [(TM)(CHL)], 555 nm for [(TM)(DDQ)] and 562 nm for [(TM)(TCNQ)] complexes. The data obtained resulted from these calculations are given in Table 2.

Plotting the values of the $(C_a^o . C_d^o / A)$ against $(C_a^o + C_d^o)$ values for each acceptor, a straight lines are obtained with a slope of 1/ε and intercept of 1/Kε as shown in Figure (3A, B and C), for the reaction mixtures of TM with CHL, DDQ and TCNQ in $CHCl_3$, respectively. The oscillator strength (f)(19-24) and the transition dipole moment (μ) of the CT-complexes(20-24), (Table 2), have been calculated from the following equations:

$f = (4.319 \times 10^{-9})\, \varepsilon_{max} \cdot \nu_{1/2}$ (1)

$\mu = 0.0958[\varepsilon_{max} \nu_{1/2} / \nu_{max}]^{1/2}$ (2)

$I_p\,(eV) = a + b(h\nu_{max})$ (3)

$E_{CT} = I_p - E_A - W$ (4)

$E_{CT} = 1243.667 / \lambda_{CT}$ (nm) (5)

Where $\nu_{1/2}$ is the band-width for half-intensit in cm^{-1}.

The dissociation energy (W) can be calculated from the corresponding CT energy (E_{CT}), donor ionization potential (I_p) and electron affinity of the acceptor (CHL, 1.37 eV and DDQ, 1.95 eV)[20-24]. The estimated value of (W) in case of DDQ as acceptor is 4.30 eV. The dissociation energy (W) of TM/CHL CT complex system can be calculated applying (equation 4), this value is 4.13 eV. The ionization potential (I_p) of the free donor of the highest filled molecular orbital on the donor was determined from the CT energies of the CT band of its complexes with CHL and TCNQ using the equations (3) [20-24]. The energy of the n-π* interaction is calculated using equation (5), where λ_{CT} is the wavelength of the CT band of the complexes; 2.25 eV (CHL), 2.24 eV (DDQ) and 2.21 eV (TCNQ).

Infrared spectra

The IR spectra of the molecular complexes of CHL, DDQ and TCNQ with TM with the molar ratio 1:1 and general formula, [(TM)(acceptor)], are shown in Figure (40A, B and C). Assignments the infrared spectral bands of the resulted CT complexes are reported in Table 3.

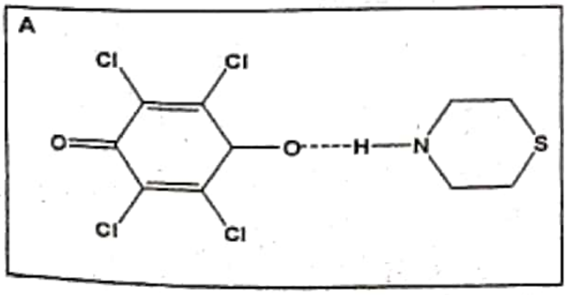
The formation of the TM/acceptor CT complexes are strongly supported by the fact that the main infrared bands for the reactants, TM and the mentioned acceptors are also observed in the reaction products spectra. Comparison of the infrared spectral bands of the free donor and acceptors (CHL, DDQ and TCNQ) with the corresponding ones appearing in the IR spectra of the CT complexes shows the following;

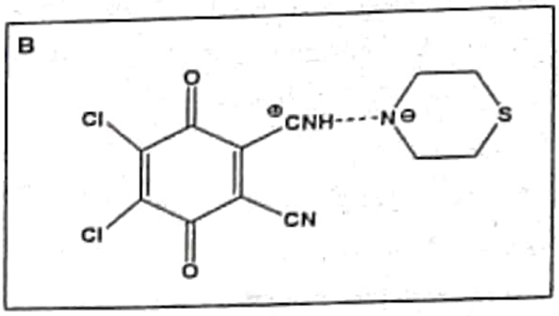
i) In the infrared spectrum of the [(TM)(CHL)] CT complex, the stretching vibration motion of the ν(NH) in case of free TM was observed at 3424 and 3300 cm^{-1} is shifted to lower wavenumber with splitting at 3420 and 3285 cm^{-1} in the IR spectrum of the TM/CHL complex upon molecular complex formation. The new band observed at ~ 3280 cm^{-1} with medium strong intensity, can be assigned to the hydrogen bonding associated between hydrogen proton of donor via the oxygen atom of one carbonyl groups of acceptor. The collected bands in the region of 3000-2800 cm^{-1} in this complex were assigned to ν_s(C-H)+ν_{as}(C-H) vibrations with the same wavenumber region compared with the free TM. The spectrum of [(TM)(CHL)] CT-complex includes a few weak/medium absorption bands located at 2620 and 2440 cm^{-1} and could be assigned to hydrogen bonding [25]. The stretching vibrational of ν(C=O) absorption band in the case of the free CHL is appeared at 1680 cm^{-1} but under complexation this band was shifted to lower value (1650 cm^{-1}). There is no doubt that, the infrared spectra are strongly supported that the CT-interaction in the case of TM/CHL complex take place through n-π* transition. As can be see, in the spectrum of [(TM)(CHL)] complex, the vibrations group of δ(N-H), ν(C-N), CNC deformation show clearly changes compared with those of free TM. The bands associated with ν(C-Cl) vibration that appeared at 903, 750 and 709 cm^{-1} in the free CHL were shifted to lower wavenumbers and decreasing in the intensities of the characteristic peaks. These shifts are indicative of a lower charge density on the chloro and a higher charge density on the carbonyl groups of CHL acceptor charge transfer complex. This phenomena proved that the complexation of (TM) with CHL takes place via the –NH group with forming the hydrogen bonding.

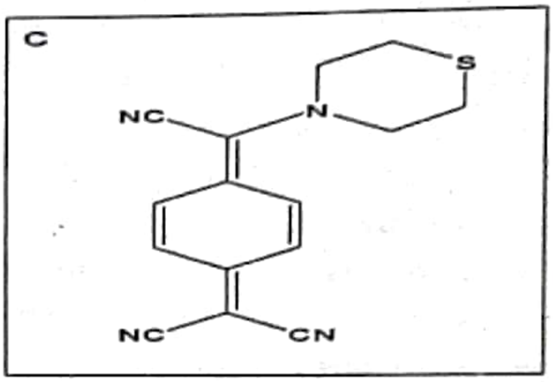
ii) In the case of [(TM)(DDQ)] CT-complex; the IR spectra of the molecular complex of DDQ with TM indicate that the ν(C≡N) and ν(C-Cl) of the free acceptor are shifted to lower wavenumber values on the complexation. Since DDQ is deprived from any acidic centers, thus we may conclude that the molecular complexes are formed through π-π* and/or n-π* charge migration from HOMO of the donor to the LUMO of the acceptor. Also, the shift of ν(C=O) of DDQ from higher to lower value on complex formation. IR spectrum of the molecular complex of DDQ with TM indicate that the single ν(C≡N) of the free acceptor molecule which exhibited at (2250 and 2231 cm^{-1}) was shifted to a lower wavenumber value (2200 cm^{-1}) while the ν(C=O) absorption band of the free DDQ at 1673 cm^{-1} was shifted to lower value (1632 cm^{-1}). Careful interpretation of IR spectra strongly supported that the CT-interaction in the case of TM/DDQ complex occurs through n-π* transition deprotonation of –NH group of TM to only one of the CN groups by forming intermolecular hydrogen bonding. In addition, the characteristic bands of the hydrogen bonding are appearing in the IR spectrum of the studied complex at ranged 2600 to 2400 cm^{-1}, this group of bands are not presented in both the free spectra of donor and acceptor.

iii) The reaction of TCNQ with the TM gives a new product. The resulting adduct is assigned the structure 7-thiomorpholino-7,8,8-tricyanoquiondimethane on the basis of a spectroscopic investigation and elemental analysis. On the other hand, the formation of TCNQ$^{\cdot-}$ radical anions has been recorded frequently. Based on these observations it can be concluded that the two new bands are due to TCNQ$^{\cdot-}$ radical anion (329 nm) and 7-thiomorpholino-7,8,8-tricyanoquion dimethane (562 nm).

In the case of [(TM)(TCNQ)] CT-complex, the IR spectrum of the solid reaction product7-thiomorpholino-7,8,8-tricyanoquiondimethane as well as band assignments are presented in the Figure 4 and Table 3. As can be seen, the CN stretching of TCNQ show a drastic shift to lower frequencies upon molecular complex formation with TM. These shifts are indicative of a higher charge density on the cyano groups of the TCNQ. The ν(CH$_2$) stretching of the TM observed in the 3000-2800 cm^{-1} region have decreasing in the intensities upon CT complexation. It is interesting to note that upon complexation of TCNQ, in the CN stretching region two bands are observed. These bands can be attributed to the CN of TCNQ$^{\cdot-}$ radical anion and the second band concerning to 7-thiomorpholino-7,8,8-tricyanoquiondimethane adduct. The N-H stretching occur as a strong broad and weak shoulder absorptions at ~ 3420 and 3300 cm^{-1} in the spectrum of free TM and at ~ 3440 cm^{-1} as medium band in the spectrum of the new adduct. These changes in the band intensities as well as wavenumber values of -N-H of the TM and the resulted adduct, proved that, the participated of –N-H group of TM in the elimination reaction (eliminated one molecule of –HCN) Scheme 1.







Scheme 1: Structures of: (A): [(TM)(CHL)], (B): [(TM)(CHL)] and (C): 7-thiomorpholino-7,8,8-tricyanoquiondimethane adducts.

Thermal investigations

Thermal analysis TGA/DTG were carried out for both [(TM)(CHL)] and 7-thiomorpholino-7,8,8-tricyanoquiondimethane adducts and discard the [(TM)(CHL)] because of the lower melting point. The thermograms are shown in Figure (5A and B) and the decomposition data are listed in Table 4.

The TG decomposition curve of the [(TM)(CHL)] CT complex is shown in Figure 5A. It gives four decomposition stages at DTG$_{max}$= 180, 245, 490 and 580°C supported by DTG data (Table 4). The first decomposition step is started from 30 till 185 °C with maximum peak at (180 °C) and corresponding to decomposition of one HCl molecule from CHL moiety with an estimated mass loss 10.65% Found (calcd. mass loss 10.46%), while the following of the second step started from 185°C to 250°C at DTG$_{max}$=245°C is accompanied by loss of 2HCl molecules with weight loss 21.00% (calcd. 20.92%). The third and fourth stages ranged 250-600 °C at maximum peaks 490 and 580 °C, respectively, involve the loss of HCl+H$_5$NSO$_2$ leaving ten carbon atoms as a residue resulting from the process of decomposition under nitrogen. The remains of ten carbon atoms confirm that the interaction between donor: acceptor occurs in 1:1 molar ratio in agreement with that obtained from the elemental analysis. The overall weight loss amounts to 65.80% (calcd. 65.62%).

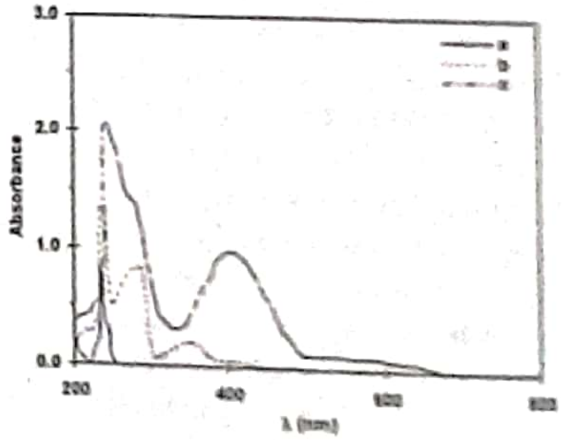
The TGA curve of the new adduct, 7-thiomorpholino-7,8,8-tricyanoquiondimethane formed from the elimination reaction between one molecule of TM and powerful acceptor, TCNQ, has four maximum peaks at 190, 335, 365 and 580 °C, and this adduct become thermally stable until 152 °C. The first decomposition steps at 190 °C without mass loss respective to the melting point of the mentioned adduct. The second and third decomposition stages occur at a maximum temperature lies in the range of 200-400°C. The weight loss associated with this stage is 30.78% and may be due to the loss of the three HCN + H_2O molecules in good agreement with the theoretical weight loss value of 29.29%. The fourth decomposition stage occurs at the maximum temperature 580°C. The found weight loss 28.98% associated with this stage can be attributed to the loss of $C_3H_{17}NS$. The theoretical value of weight loss associated with the loss of these species, 29.29% are very near to the found value. The final thermal products obtained as a residue are proposed to be a 13C. The agreement between the theoretical and found weight of the residue gives a good support to the proposed mechanism.

Kinetic studies

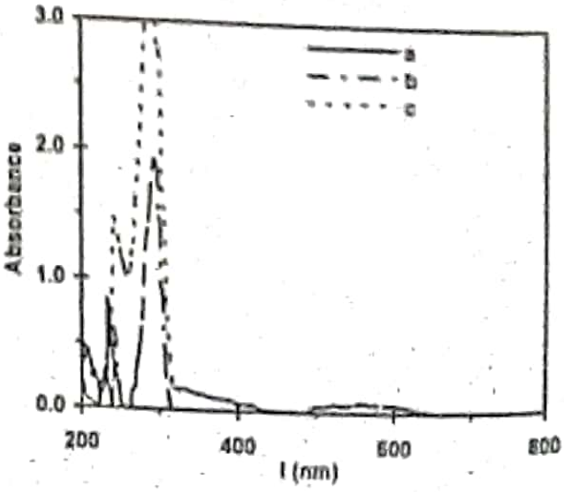
On the basis of the above thermal decomposition, the kinetic analysis parameters such as activation energy, E^*, enthalpy of activation, ΔH^*, entropy of activation, ΔS^*, and free energy change of decomposition, ΔG^*, were evaluated graphically by employing the commonly two methods of Coats and Redfern (26) as well as the approximation method of Horowitz and Metzger (27).

In our investigation the general thermal behaviors of the two TM CT complexes in terms of stability ranges, peak temperatures and values of kinetic parameters, are shown in Fig. 6 and Table 5. The linearization plots, confirms the first order kinetics for the decomposition process. Kinetic parameter shows that the decomposition follows first order kinetics and proceeds in two step decomposition. According to the kinetic data obtain from the TG curves; the activation energy relates the thermal stability of the metal complexes. Among CT complexes, activation energy increases as [(TM)(CHL)]>7-thiomorpholino-7,8,8-tricyanoquiondimethane adduct. The two CT complexes have negative entropy, which indicates that the complexes are form spontaneously. The negative value of entropy also indicates a more ordered activated state that may be possible through the chemisorption of oxygen and other decomposition products. The negative values of the entropies of activation are compensated by the values of enthalpies of activation, leading to almost the same values for the free energy of activation.

(A)



(B)



(C)

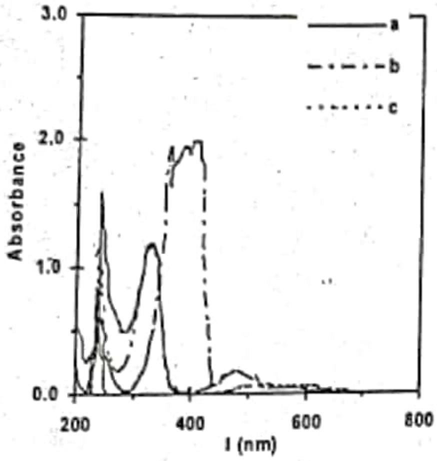
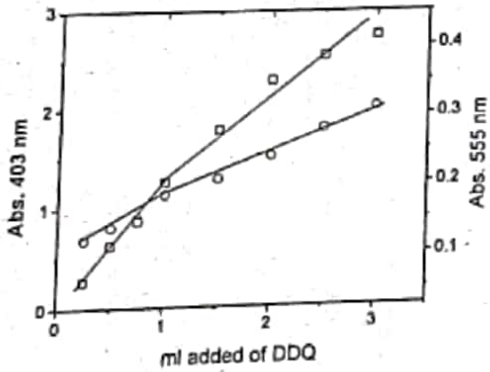


Fig. 1: Electronic absorption spectra of; (A): TM//DDQ, (B): TM/CHL and (C): TM/TCNQ reactions in CHCl$_3$ (a) = donor (1.0x10^{-4}M), (b) = acceptor (1.0x10^{-4}M) and (c) = CT-complex

(A)



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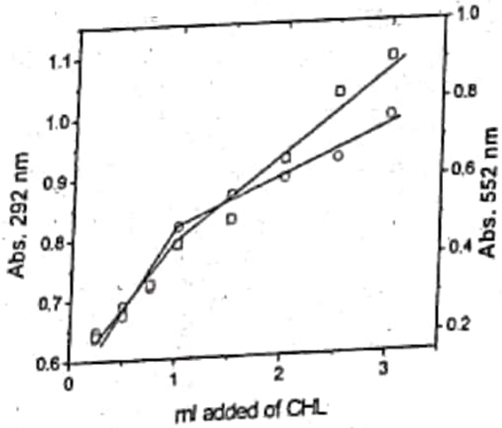


(C)

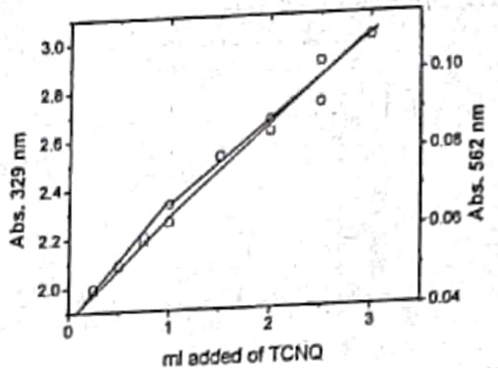
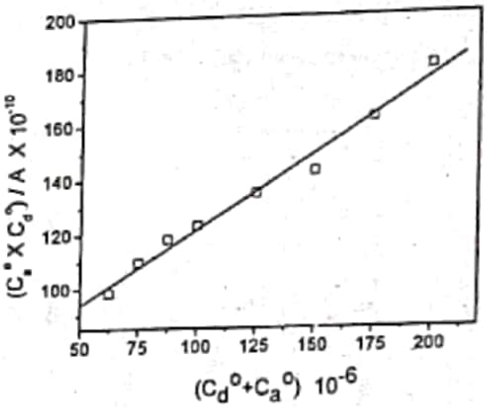
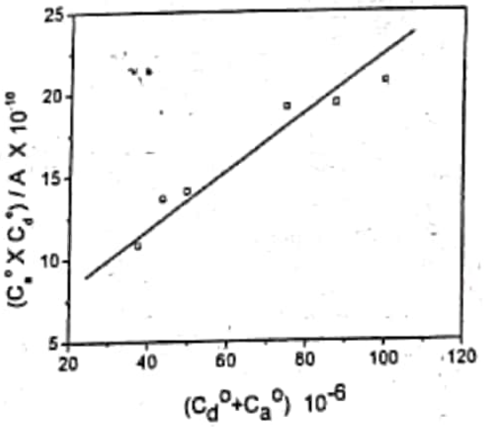


Fig. 2: Photometric titration curves for: (A): TM/DDQ, (B): TM/CHL and (C): TM/TCNQ systems in CHCl$_3$ at (o=403, □=555 nm), (o=292, □=552 nm) and (o=329, □=562 nm), respectively.

(A)



(B)



(C)

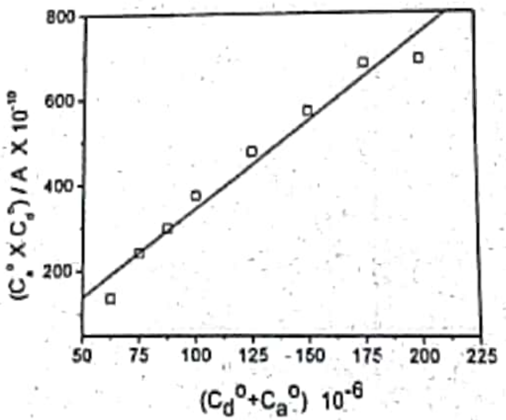


Fig. 3: The plot of ($C_d^o+C_a^o$) against $C_d^o.C_a^o/A$, for the (A): [(TM)(DDQ)], (B): [(TM)(CHL) and (C): [(TM)(TCNQ)] CT-complexes at 555, 552 and 562 nm, respectively.

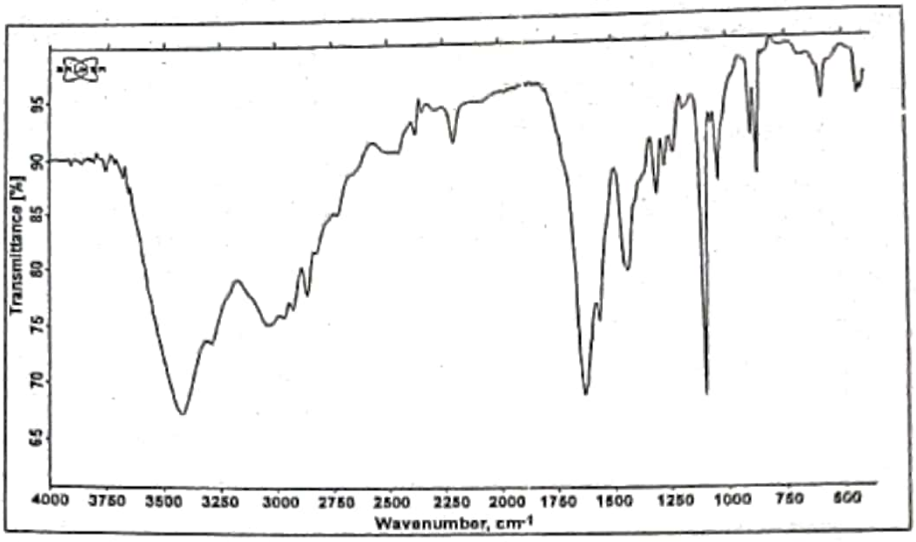


Fig. 4A: Infrared spectra of; [(TM)(DDQ)] complex.

(B)

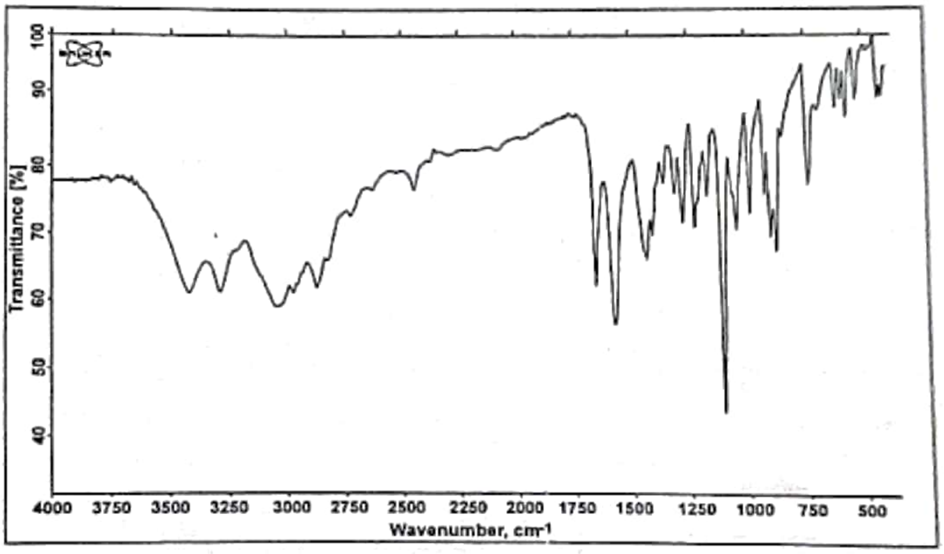


Fig. 4B: Infrared spectra of; [(TM)(CHL)] complex.

(C)

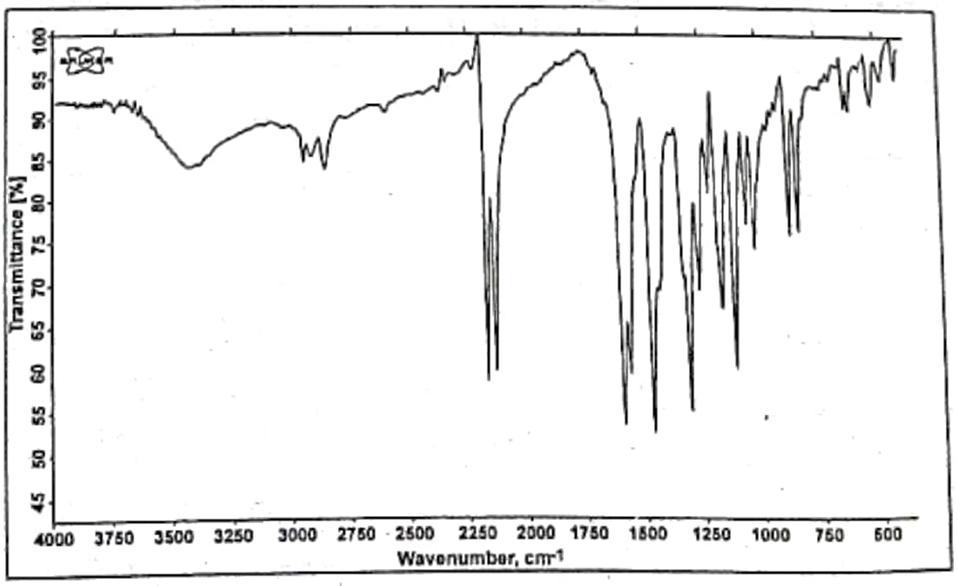


Fig. 4C: Infrared spectra of: 7-thiomorpholino-7,8,8-tricyanoquiondimethane compounds.

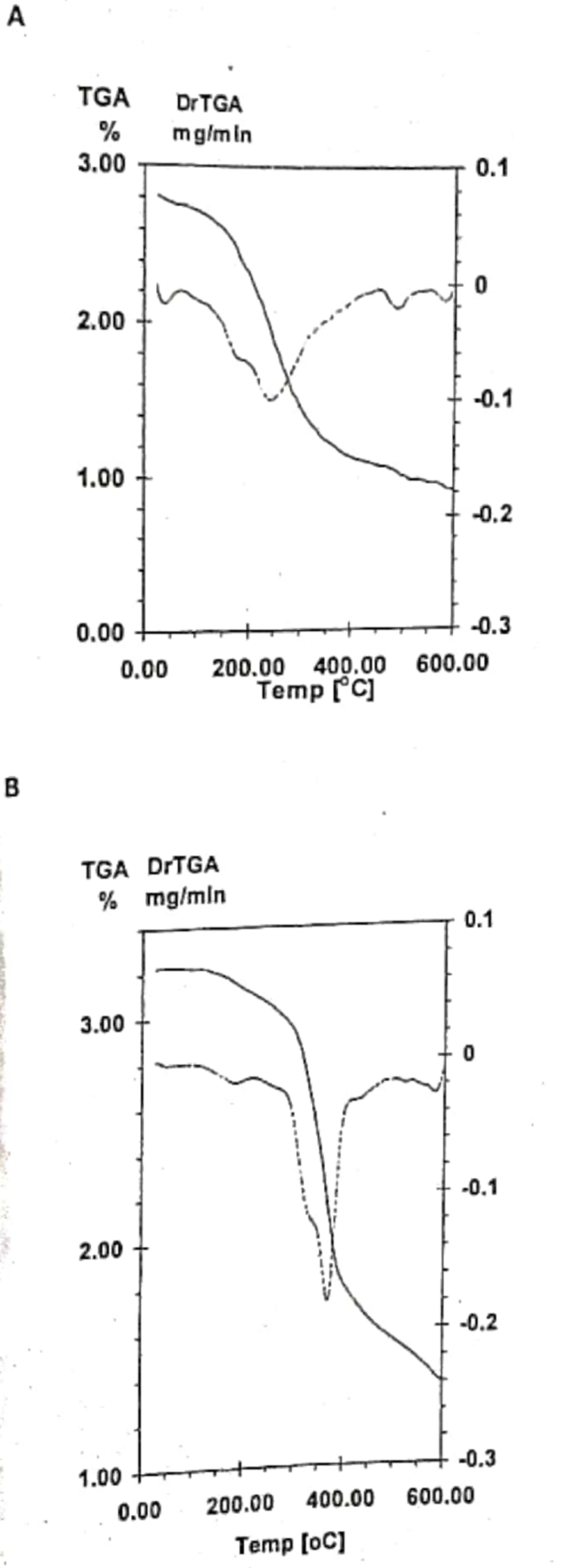


Fig. 5: TGA/DTG thermal diagram of: (A): [(TM)(CHL)] and (B): 7-thiomorpholino-7,8,8-tricyanoquiondimethane compounds.

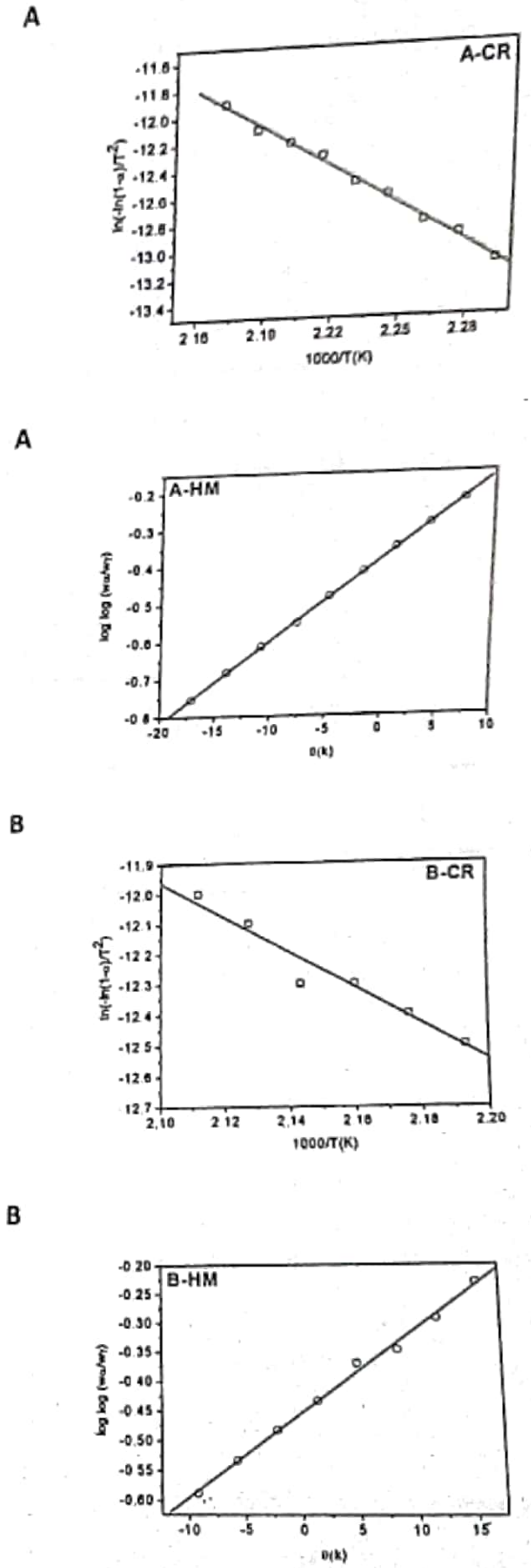


Fig. 6: Kinetic diagrams of Coats Redfern (CR) and Horowitz-Metzger (HM) equations for (A): [(TM)(CHL)] and (B): 7-thiomorpholino-7,8,8-tricyanoquion dimethane compounds

Table 1: Elemental analysis CHN and physical parameters data of the CT-complexes formed in the reaction of the TM with DDQ, CHL and TCNQ.

CT Complexes (FW)	Mwt	C%		H%		N%		Physical data	
		Found	Calc.	Found	Calc.	Found	Calc.	Color	mp (°C)
[(TM)(DDQ)] ($C_{12}H_9N_3Cl_2O_2$)	330	43.53	43.64	2.69	2.73	12.66	12.73	brown	~ 45
[(TM)(CHL)] ($C_{10}H_9NCl_4SO_2$)	349	34.27	34.38	2.55	2.58	3.90	4.01	brown	166
[(TM)(TCNQ)] ($C_{19}H_{22}N_4S$)	338	67.42	67.46	6.47	6.51	16.44	16.57	green	194

Table 2: Spectrophotometric results of the CT-complexes of (A): [(TM)(CHL)], (B): [(TM)(DDQ)] and (C): [(TM)(TCNQ)] CT-complexes.

Complex	λ_{max} (nm)	E_{CT} (eV)	K x 10^4 ($l.mol^{-1}$)	ε_{max} x 10^4 ($l.mol^{-1}.cm^{-1}$)	f	μ	I_p
A	552	2.25	3.83	5.62	2.70	56.80	7.78
B	555	2.24	8.34	1.81	0.97	33.90	8.51
C	562	2.21	6.37	0.246	1.33	12.60	6.67

Table 3: Infrared frequencies[(a)] (cm^{-1}) and tentative assignments for [(TM)(CHL)], [(TM)(DDQ)] and [(TM)(TCNQ)] complexes.

TM and their CT-complexes				Assignments(b)
TM	DDQ	CHL	TCNQ	
3415 3303	3423 3307	3416 3285	3412	ν(N-H)
3040 2862 2819 2723	3037 2975 2928 2864 2750	3042 2970 2872	3011 2955 2920 2864	νs(C-H) +νas(C-H)
2625 2516 2435	2712 2625 2448	2725 2622 2440	---	Hydrogen bonding
–	2202	---	2170 2132	ν(C≡N)
1648	1623	1650	---	ν(C=O) +ν(C=N); δdef(N-H) Ring breathing bands
1562 1422	1564 1437	1574s 1432s 1405	1591 1562 1466	ν(C=C) C-H deformation
1353 1302 1222 1185 1100 1040	1308 1272 1234 1188 1105 1069 1041	1355 1303 1272 1222 1161 1101 1040	1312 1262 1224 1170 1113 1061 1025	ν(C-C) + ν(C-N) + ν(C-O-C) CH, in-plane bend
890 870 820	898 872 846	982 920	963 951 924 874 845	δrock; NH CH-deformation ν(C-Cl)
663 584 432 414	592 439 421	897 873 736 614 595 572 527	697 633 615 526 487 489 421	skeletal vibration CH bend CH out of plane bend Skeletal vibration CNC def.

(a): s = strong, w = weak, m = medium, sh = shoulder, v = very, br = broad. (b): ν, stretching; ν, bending.

Table 4: Thermal analysis results for the (A): [(TM)(CHL)] and (B): 7-thio morpholino-7,8,8-tricyanoquiondimethane compounds.

Complex	Stage	TGA range/ (°C)	DTG$_{max}$ / (°C)	Weight loss(%)		Evolved moiety
				Found	Calc	
A	I	30-185	180	10.65	10.46	HCl
	II	185-250	245	21.00	20.92	2HCl
	III, IV	250-600	490, 580	34.15	34.24	HCl + H_5NSO_2
	Residue					10C
B	I	30-200	190	--	--	Mp
	II, III	200-400	335, 365	30.78	29.29	3HCN + H_2O
	IV	400-600	580	28.98	29.29	$C_3H_{17}NS$
	Residue					13C

Table 5: Kinetic parameters of the (A): [(TM)(CHL)] and (B): 7-thiomorpholino-7,8,8-tricyanoquiondimethane compounds.

complex	stage	method	parameter					r
			E (J mol^{-1})	A (s^{-1})	ΔS (J mol^{-1} K^{-1})	ΔH (J mol^{-1})	ΔG (J mol^{-1})	
A	1st	CR	7.8×10^4	2.00×10^7	-1.05×10^2	7.60×10^4	1.24×10^5	0.9954
		HM	7.6×10^4	1.00×10^8	-9.0×10^1	8.19×10^4	1.22×10^5	
	2nd	CR	6.88×10^4	3.05×10^4	-1.63×10^2	6.43×10^4	1.40×10^5	0.9977
		HM	7.26×10^4	1.80×10^5	-1.45×10^2	6.80×10^4	1.43×10^5	
B	1st	CR	4.80×10^4	1.64×10^3	-1.84×10^2	4.48×10^4	1.33×10^5	0.9880
		HM	5.64×10^4	2.25×10^4	-1.65×10^2	5.32×10^4	1.29×10^5	
	2nd	CR	1.50×10^5	7.90×10^{10}	-4.20×10^1	1.40×10^5	1.73×10^5	0.9997
		HM	1.70×10^5	8.66×10^{12}	-3.12×10^1	1.64×10^5	1.66×10^5	

*Units of parameters: E in Jmole^{-1}, A in s^{-1}, ΔS in Jmole^{-1}k^{-1}, ΔH and ΔG in Jmole^{-1}

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دراسات طيفية وحرارية على متراكبات انتقال الشحنة لثيومورفولين مع بارا كلورانيل و ٢،٣-ثنائي كلورو-٥،٦-ثنائي سيانو-١،٤-بنزوكينون و ٧،٧،٨،٨-رباعي سيانوكينو داي ميثان

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حضرت متراكبات انتقال الشحنة الى ثيومورفولين (معطى للالكترونات) مع كلا من بارا كلورانيل و ٢،٣-ثنائي كلورو-٥،٦-ثنائي سيانو-١،٤-بنزوكينون و ٧،٧،٨،٨-رباعي سيانوكينو داي ميثان (مستقبل للالكترونات) بنسبة ١:١ .

و قد تمت دراسة هذه المتراكبات باجراء التحليل العنصري لها و قياس أطياف الامتصاص الترددي و الالكتروني و ايضا اجراء تحليل حراري للمتراكبات الصلبة و تم التعرف على الطبيعة الكيميائية للمتراكبات الصلبة و طبيعة تكوينها و تركيبها.

و أجريت دراسة تفصيلية لجميع الامتصاصات الترددية لكل المتراكبات ، وتختلف الامتصاصات الترددية للمتراكبات الناتجة عن امتصاصات المتفاعلات مما يدل على تكوين هذه المتراكبات . حيث تظهر الامتصاصات الالكترونية للمتراكبات الجديدة مختلفة عن الامتصاصات الفردية لكلا من المعطى و المستقبل مما يدل على تكوين المتراكبات الجديدة . و قد عزى هذا الامتصاص الى الانتقال الالكتروني C-T و أن المتراكبات الناتجة تكون بنسبة ١:١ (acceptor :donor) اهتمت الدراسة ايضا بالتحليل الحراري لكلا من المتراكبين [(TM) (DDQ)] و [(TM) (TCNQ)] بهدف تحديد و تأكيد التراكيب و طبيعة الترابط في هذه المتراكبات . أما المتراكب [(TM) (CHL)] لم يجرى عليه تحليل حراري نظرا لانخفاض درجة انصهاره .

تم حساب ثابت التكوين K و معامل الامتصاص ε و طاقة التكسير لهذه المتراكبات و باستخدام التحليل الحراري تم حساب المعاملات الثرموديناميكية E , ΔH , ΔS, ΔG .