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Intermolecular hydrogen bond complexes by *in situ* charge transfer complexation of o-tolidine with picric and chloranilic acids

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ABSTRACT

A two new charge transfer complexes formed from the interactions between o-tolidine (o-TOL) and picric (PA) or chloranilic (CA) acids, with the compositions, $[(o-TOL)(PA)_2]$ and $[(o-TOL)(CA)_2]$ have been prepared. The ¹³C NMR, ¹H NMR, ¹H-Cosy, and IR show that the charge-transfer chelation occurs *via* the formation of chain structures O-H···N intermolecular hydrogen bond between 2NH₂ groups of o-TOL molecule and OH group in each PA or CA units. Photometric titration measurements concerning the two reactions in methanol were performed and the measurements show that the donor-acceptor molar ratio was found to be 1:2 using the modified Benesi-Hildebrand equation. The spectroscopic data were discussed in terms of formation constant, molar extinction coefficient, oscillator strength, dipole moment, standard free energy, and ionization potential. Thermal behavior of both charge transfer complexes showed that the complexes were more stable than their parents. The thermodynamic parameters were estimated from the differential thermogravimetric curves. The results indicated that the formation of molecular charge transfer complexes is spontaneous and endothermic.

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1. Introduction

The charge transfer interactions of significant interactions, which have many applications in various fields, therefore, received considerable attention in recent years by many researchers [1–5]. CT complexes have applications in many fields such as electronics, solar cells [6], optical devices and electrical conductivities [7]. Charge transfer complexes have also been recognized as an important phenomenon in drug receptor binding mechanism and in many biological processes like photosynthesis and oxidative processes [8]. The charge transfer reactions have successfully utilized in pharmaceutical analysis as given the drug (donor) with different acceptors [9–12].

o-Tolidine (Formula I) is slightly soluble in water and has a melting point of 129 °C. It readily forms salts with acids [13]. o-Tolidine is a commercially important aromatic amines used mainly for dye production, but also for the production of certain elastomers. o-Tolidine is an intermediate for the production of soluble azo dyes and insoluble pigments used particularly in the textile, leather and paper industries [14]. Also it is widely used as a reagent or indicator

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in analytical, clinical and forensic chemistry, such as in the analytical determination of gold. Numerous studies have been [15,16] devoted to aromatic amines suspected of having mutagenic or carcinogenic properties.



In continuation of our aimed studies on such type of interactions [17–20], herein this paper was reported the spectral tools in order to investigate the intermolecular hydrogen bond of the charge transfer complexes of o-tolidine (o-TOL) with picric (PA) and chloranilic (CA) acids. A literature survey reveals that no work on the formation of charge transfer complexes between otolidine and either PA or CA acids have been investigated. In view of this, we described the synthesis and spectroscopic characterizations such as UV–vis, FT-IR, ¹H NMR, ¹³C NMR and ¹H-Cosy in the present study to interpretative the mechanism of interaction of o-tolidine with PA and CA acceptors. To track the status of the thermal stability of charge transfer complexes formed the thermo gravimetric/differential thermo gravimetric analysis and kinetic thermodynamic parameters (E^* , ΔS^* , ΔH^* and ΔG^*) were employed.

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2. Experimental

o-Tolidine (o-TOL) was of analytical reagent grade (Aldrich Co.). Both π -acceptors (PA and CA) were purchased from Aldrich. Stock solutions of o-TOL and acceptors were freshly prepared and the spectroscopic grade methanol (BDH) was used as received.

2.1. Synthesis of o-TOL/PA and o-TOL/CA charge-transfer complexes

The two solid CT-complexes of o-TOL with PA or CA were prepared by mixing a saturated solution of the o-TOL donor in 10 ml MeOH to each of saturated solutions of PA or CA in the same solvent with continuously stirring for about 45 min at room temperature. The solutions were allowed to evaporate slowly at room temperature, the resulted complexes in the solid state filtered and washed several times with little amounts of solvent, and dried under vacuum over anhydrous calcium chloride. Charge-transfer complexes of o-TOL/PA formed with empirical formula $C_{26}H_{20}N_8O_{14}$ with molecular weight 670.5 g/mol and o-TOL/CA formed with empirical formula $C_{26}H_{20}N_2Cl_4O_8$ with molecular weight 630.3 g/mol.

[(o-TOL)(PA)₂]: Color: yellow, yield: 84%, Calc. (%): C=46.53%, H=3.28% and N=16.70%, Found (%): C=46.34%, H=3.21% and N=16.47%.

[(o-TOL)(CA)₂]: Color: violet, yield: 87%, Calc. (%): C=49.50%, H=3.17% and N=4.44%, Found (%): C=49.27%, H=3.13% and N=4.35%.

2.2. Analysis

The electronic UV-vis. spectra of the o-TOL, PA, CA and the resulted CT complexes were recorded in the region of (200-800 nm) by using a Jenway 6405 Spectrophotometer with quartz cells, 1.0 cm path in length. IR measurements (KBr discs) of the o-TOL, acceptor and both CT complexes were carried out on a Bruker FT-IR spectrophotometer (400–4000 cm⁻¹). The NMR spectra were obtained on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ¹H and ¹³C, respectively using a dual 5 mm probe head. The measurements were carried out in DMSO-d₆ solution at ambient temperature. The chemical shift was referenced to tetramethylsilane (TMS), standard experiments with 30° pulses, 1 s relaxation delays, 16 K time domain points, zero-filled to 64 K for protons and 32 K for carbons were performed. The distortionless enhancement by polarization transfer (DEPT) spectra were recorded under the same conditions as the ¹³C NMR spectra and $\tau = (2^{1}J_{CH}) - 1 = 3.45 \,\mu s$ was used. The 2D ¹H/¹H correlated spectra (COSY) were performed with spectral width 2200 Hz, relaxation delay 2 s, number of increments 512, and size 1 K × 1 K. The 2D ¹H/¹³C heteronuclear multiple quantum coherence (HMQC) experiments were carried out with a spectral width of 2200 Hz for ¹H and 9000 Hz for 13 C, relaxation delay 1.5 s, FT size 1 K \times 256 W. 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.

3. Results and discussion

3.1. UV-vis spectral studies

UV–vis absorption spectra of o-TOL/PA and o-TOL/CA CT-complexes were scanned in MeOH solvent. The concentration of o-TOL in the reaction mixture was kept fixed at $1.0\times10^{-4}\,M$ in MeOH solvent, while, the concentration of PA or CA was changed from $0.25\times10^{-4}\,M$ to $4.0\times10^{-4}\,M$. These concentrations were



Fig. 1. Electronic absorption spectra of o-TOL/CA and o-TOL/PA reactions in MeOH.

covered along the range from 1:0.25 to 1:4.00. The UV-vis spectra of o-TOL/PA and o-TOL/CA systems were shown in Fig. 1A and B. The measured spectra were detected definite absorption bands which are not existed in both spectra of the free donor and acceptors. These bands are noticed at (352 and 419 nm) and (335 and 532 nm) due to CT-complexes formed from the reactions of o-TOL with PA and CA, respectively. Photometric titration curves based on charge transfer bands are shown in Fig. 2A and B. These photometric titration curves were obtained according to well known method [21] and it is refereed to formation of 1:2 CT complexes. The 1:2 Eq. (1) [22] was used in the calculations.

$$\frac{C_A^{\circ 2} C_D^{\circ}}{A} = \frac{1}{K\varepsilon} + \frac{1}{\varepsilon} \cdot C_A^{\circ} (4C_D^{\circ} + C_A^{\circ})$$
(1)

where $C_A^{\circ 2}$ and C_2° are the initial concentration of the π -acceptor (PA and CA) and donor (o-TOL), respectively, and *A* is the absorbance of the detected CT-band. The data obtained C_D° , $C_A^{\circ 2}$, $C_A^{\circ}(4C_D^{\circ} + C_A^{\circ})$ and $(C_A^{\circ 2}, C_D^{\circ})/A$ in methanol were calculated. By plotting $(C_A^{\circ 2}, C_D^{\circ})/A$ values vs $C_A^{\circ}(4C_D^{\circ} + C_A^{\circ})$, straight lines were obtained with a slope of $1/\varepsilon$ and an intercept of $1/k\varepsilon$ as shown in Fig. 3A and B.

The oscillator strength f was obtained from the approximate formula [23].

$$f = (4.319 \times 10^{-9})\varepsilon_{\max}.v_{1/2} \tag{2}$$

where $v_{1/2}$ is the band-width for half-intensity in cm⁻¹ and ε_{max} is the maximum extinction coefficient of the CT-band. The oscillator strength values are given in Table 1. The data resulted reveals



Fig. 2. Photometric titration curves for the o-TOL/CA and o-TOL/PA systems at 532 and 419 nm, respectively.

several items. (i) The o-TOL/PA and o-TOL/CA systems show high values of both formation constant (K) and molar absorptivity (ε). This high value of (K) reflects the high stability of the o-TOL complexes as a result of the expected high donation of the o-TOL which contains two of amino and methyl groups. (ii) The different values of the oscillator strength, f, increases with increasing in the dielectric constant (D) of the solvent. This result could be explained on the basis of competitive solvent interactions with the acceptors [24,25].

The transition dipole moment (μ) of the o-TOL CT-complexes, Table 1, has been calculated from Eq. (3) [26];

$$m(\text{Debye}) = 0.0958 [\varepsilon_{\text{max}} v_{1/2} / v_{\text{max}}]^{1/2}$$
 (3)

The transition dipole moment is useful for determining if transitions are allowed, that the transition from a bonding π orbital to an antibonding π^* orbital is allowed because the integral defining the transition dipole moment is nonzero.

The ionization potential (I_p) of the o-TOL donor in the charge transfer complexes of (o-TOL/PA and o-TOL/CA) are calculated using empirical equation derived by Aloisi and Piganatro Eq. (4)

Table 1



Fig. 3. The plot of C_d° ($4 C_d^{\circ} + C_a^{\circ}$) values against ($C_d^{\circ 2} \cdot C_a^{\circ}$ /A) values for the o-TOL/CA and o-TOL/PA systems at 532 and 419 nm, respectively.

[27,28];

$$ID(ev) = 5.76 + 1.53 \times 10^{-4} v_{\rm CT} \tag{4}$$

where ν_{CT} is the wavenumber in cm⁻¹ corresponding to the CT band formed from the interaction between donor and acceptor. The electron donating power of a donor molecule is measured by its ionization potential which is the energy required to remove an electron from the highest occupied molecular orbital.

The energy of the charge-transfer complexes E_{CT} of the o-TOL complexes is calculated using Eq. (5) [26];

$$E_{\rm CT} = (h\nu_{\rm CT}) = 1243.667/\lambda_{\rm CT} \ (\rm nm) \tag{5}$$

where, λ_{CT} is the wavelength of the complexation band.

Determination of resonance energy (R_N) [29] theoretically derived from (Eq. (6));

$$\varepsilon_{\rm max} = \frac{7.7 \times 10^{-4}}{h \nu_{\rm CT} / [R_{\rm N} - 3.5]} \tag{6}$$

where ε_{max} is the molar absorptivity of the CT-complexes at maximum CT band, ν_{CT} is the frequency of the CT peak and R_N is the resonance energy of the complex in the ground state, which, obviously is a contributing factor to the stability constant of the complex (a ground state property). The values of R_N for the (PA and CA) complexes under study have been given in Table 1.

Spectrophotometric results of the o-TOL CT-complexes; (A) [(o-TOL)(CA)] and (B) [(o-TOL)(PA)].

Complex	$\lambda_{max}\left(nm ight)$	$E_{\rm CT}~({\rm eV})$	$K(l \operatorname{mol}^{-1})$	$\varepsilon_{\rm max}~(l{\rm mol^{-1}}{\rm cm^{-1}})$	f	μ	I_p	D	R_N	$\Delta G^{\circ}(25 \circ \text{C}) (\text{KJ mol}^{-1})$
А	532	2.34	0.073×10^{10}	0.1314×10^{6}	45.40	71.64	8.64	33	0.572	6.48×10^{13}
В	419	2.97	0.112×10^{10}	0.1143 × 10 ⁶	49.37	66.30	9.41	33	0.711	5.43×10^{13}

The standard free energy changes of complexation (ΔG°) were calculated from the formation constants by the following Eq. (7) [30];

$$\Delta G^{\circ} = -2.303 RT \log K_{\rm CT} \tag{7}$$

where ΔG° is the free energy change of the CT-complexes (KJ mol⁻¹), *R* is the gas constant (8.314 J mol⁻¹ K), *T* is the temperature in Kelvin degrees (273+°C) and *K*_{CT} is the formation constant of the complexes (1 mol⁻¹) in different solvents at room temperature.

3.2. Infrared spectral studies

Infrared spectral studies sheds light on the place of donation in donor species and the differences occurs in the spectra of both PA and CA charge transfer complexes. Comparison between the spectra of both CT-complexes and the data of o-TOL donor and receptors have been studied and recorded in Table 2. The full spectra of o-TOL/CA and o-TOL/PA were shown in Fig. 4A and B.

If we take into account the changes that have taken place in the region of $4000-3000 \text{ cm}^{-1}$, we find that this area includes some stretching vibration motions; the ν (OH) group of CA and PA accep-

tors, ν (N–H) of NH₂ group of o-TOL donor and some of stretching motions of ν (C–H) respected to the aromatic rings.

3412 s + 3375 s + 3338 ms (o-TOL free donor) → 3414 vw + 3386 w + 3357 vw(o-TOL/CA complex) 3400 s + 3328 s (o-TOL/PA complex)

Found that the values characteristic of both the –OH and the –NH₂ groups happened to shifted to a lower values and also decreased in the intensities of vibration motions, which indicates that the interactions placed among the –OH group of each of CA and PA and –NH₂ group of o-TOL through the hydrogen bonding (region 3000–2000 cm⁻¹) existed at 2757 sh, 2643 w, 2571 w for o-TOL/CA and 2728 vw, 2657 vw, 2571 w, 2543 w for o-TOL/PA. These new bands were attributed to the stretching vibration of a proton attached to the donation site (–NH₂) of the donor and forming ⁺NH₃ group [31]. These results caused by the protonation of both NH₂ group of the o-TOL donor through one protons transfer from the acidic center on the CA or PA acceptors *via* –OH group to the basic center on the donor NH₂ group.

To place greater emphasis on the interactions between the donor and both acceptors, the 2000–1000 cm⁻¹ region was investigated. This region contain the bending vibration motions of $-NH_2$ group ($\delta(NH_2)$) which influenced by charge transfer complexation

Table 2

Infrared frequencies^a (cm⁻¹) and tentative assignments for o-TOL, CA, PA, [(o-TOL)(CA)], and [(o-TOL)(PA)] CT-complexes

9475 s 9412 s 3415 s3420 s, br3416 br3471 w3400 w9400 s 100 mS1471 w3400 s 100 mS3400 s 100 mS1471 w3400 s 100 mS1470 s 100 mS1471 w3400 s 100 mS1471 w1471 w	o-TOL	CA	PA	o-TOL/CA	o-TOL/PA	Assignments ^b
3412 s 3475 s3235 s, br3103 ms3144 wv328 sv(N-H); NH23375 s338 ms3367 w3381 ms337 s-3213 ms337 sw3019 m-2870 w3114 shw3019 m-2870 w290 nbvv(C-H); Ch, 100 matic rings2940 msv2957 vw296 vwv(C-H); Ch, 100 matic rings2940 msv2957 vw295 vwvu(C-H); Ch, 100 matic rings2940 msv2957 vw295 vwvu(C-H); Ch, 100 matic rings2940 msv2957 vw2857 vw100 matic rings2860 ms2957 vw2857 vw100 matic rings2870 ms1664 ms1861 ms1618 s1614 vs0vcrtone of (CH)1655 vs1652 vs1652 vs1557 svu(NO2); PA1650 ms1563 vs1563 vs1568 s1286 s0vcrtone of (CH)1655 s1563 vs1618 s1614 vs0vcrtone of (CH)1654 ms1562 vs157 svu(NO2); PA1550 w1520 vs158 s128 s128 s1550 w159 s128 s128 s0vcrtone of (CH)1520 w150 s126 s128 s128 s1520 w150 s128 s128 s128 s1520 w150 s128 s128 s128 s1520 s150 s128 s128 s128 s<	3475 s	3420 s,br	3416 br	3471 vw	3400 s	ν(Ο-Η)
3375 s3386 w3387 w3378 m3213 ms-2580 sh3143 sh2200 sbrv.(C-H); aromatic rings3213 ms-2872 w3057 w3057 w3019 m-2872 w3057 w3057 w2982 ms-2957 vs, Dr2966 vwv.a(C-H); CH12982 ms-2957 vs, Dr2957 vs, Dr2857 vs, Dr2856 w-2857 vs, Dr2857 vs, Dr2857 vs, Dr2856 w-2613 vs, Dr2814 vw2920 vmv.a(C-H); CH12856 w-2613 vs, Dr2814 vw2814 vw2814 vw2856 w2613 vs, Dr2814 vw100 sr2856 w2613 vs, Dr2814 vw100 sr2856 w1664 ms1861 ms1618 s1614 vs, Dr100 sr1870 ms1660 vs1832 vs1485 vs1557 sv.a(N0); PA1520 v1680 vs1529 vs1486 vs386 sr386 sr1520 v1282 vs1428 vw1400 sa(CH1) v for Or)1848 m1368 s1363 vs1312 w1367 srv(C-P) + v(-C)1295 s1168 v1263 vs1386 sr1386 sr1367 srv(C-P) + v(-C)1295 s1168 vs1263 vs1363 vs1362 sr137 sr114 sr1294 sr1263 vs1263 vs1363 sr121 sr126 sr1394 sr168 sr1432 sr126 sr136 sr121 sr1395 sr168 sr136	3412 s	3235 s, br	3103 ms	3414 vw	3328 s	ν (N–H); NH ₂
338 ms 3213 ms 3019 m335 rw3357 rw 3143 sh3200 shr 3200 shrv(C-H) cmatic ings3213 ms 3019 m-2880 w3143 sh3200 shrv(C-H) cmatic ings2814 ms-2872 w3057 wv(C-H) cmatic ings282 ms2957 vw2986 wwv(C-H) cmatic ings2840 mw-2987 vs, p2857 wv(C-H) cmatic ings2888 w-2877 vs, p2857 vw2857 vw2886 w-2757 sh2728 vwHydrogen bonding2850 w2757 sh2728 vwHydrogen bonding2643 w2657 vw2571 w2643 w2657 vw1620 vs1650 w1660 vs1661 sv1664 vs0vertone of a/(H)1652 sv1660 vs1668 vs1485 vs1578 sv(C-0) + v(C-1)1574 s1660 vs1668 vs1428 vw1405 s1(C-0)1574 s1269 vs1386 s1386 s1366 sv(C-0) + v(C-1)158 s1368 s1428 vw1300 vs1342 wInplane bending128 s1168 w1263 w1300 vs1328 s1164 s1164 s128 s1168 w1214 s1214 s1171 s1174 s129 s1164 s1214 s1214 s1141 s1141 s129 s1168 w171 s1174 s1174 s129 s1168 w1614 sv00 m86 sAromatic rings vibrations of ortho substituted129 s1168 w129 s<	3375 s	,		3386 w		
3213 ms 3019 m-280 sh 2872 w3143 sh 2872 w200 m 2014 w114 sh 2057 w114 sh 2057 w2982 ms 2940 mw2957 vm 2914 vw2989 vw 2929 vwvs(C-H); CH3 vs(C-H); CH32840 mw 2940 mw-2877 vsb 2877 vsb2929 vw 2929 vw 2929 vm 2814 vw100 mm 2014 vm2886 w 2886 w2877 vsb 2757 sh 2757 vh 2757 vm 2571 w2787 vm 2571 w2870 ms1664 ms1861 ms1618 s1614 vs 1557 s0 vortno of A(H)1652 vs 1574 s1630 vs1632 vs1618 s1557 s 1485 vmvs(Mo2); PA1654 ms1861 ms1618 s1557 s 1485 vmvs(Mo2); PA1570 w1520 vs1529 vs1485 vm1608 vs1528 s 1486 vm1584 s1263 vs1343 ms1366 s1386 s 1412 vm1317 sm1384 s1263 vs1343 ms1368 s1414 vm129 vs1150 ms1214 s1328 v 1143 vm1414 sm129 vs1150 ms1214 s1217 vs 1141 sm129 vs1130 ms1214 s1217 vs1065 s1143 vm1217 vs1043 sm1214 sm1050 s1143 vm1217 vs 1141 sm114 sm1050 s1143 vm1217 vs1043 sm1050 s1143 vm1217 vs1043 sm1050 s1143 vm1217 vs1043 sm1050 s1143 vm1217 vs1043 sm1050 s11	3338 ms			3357 vw		
	3213 ms	_	2980 sh	3143 sh	3200 s.br	v(C-H): aromatic rings
2982 ms - - - 2957 vw 2957 vw 2940 mw - 2914 vw 2929 vw $v_{a}(C-H); CH_3$ 2886 w - 2857 vsbr 2857 vw 2886 w - 2857 vsbr 2857 vw 2886 w - 2643 vw 2657 vw 2870 ms 1664 ms 1861 ms 1618 s 1614 vs Overone of $\delta(CH)$ 1870 ms 1664 ms 1661 ms 1618 s 1614 vs Overone of $\delta(CH)$ 1870 ms 1630 vs 1632 vs 1485 vs 1528 s $v_a(NO_2): PA$ 1870 ms 1664 ms 1608 vs 1518 s 1544 vs Overone of $\delta(CH)$ 1870 w 1630 vs 1432 s 1485 vs 1528 s $v_a(NO_2): PA$ 1870 ms 1664 ms 1618 s 1514 vs Overone of $\delta(CH)$ No 1870 ms 1632 vs 1432 vs 1488 vs $v_a(C-H) + v(C-C)$ No 1870 ms 1680 ms 1438 vs 1386 s 1386 s $v_a(C+H) + \delta_a(CH_3) + \delta_a(CH_3)$ 1280 vs 1263 vs 1263 vs 1386 s	3019 m		2872 w		3114 sh	· (- · ·),
1980 ms 2940 ms2957 vs 2914 vv 2929 vs 2929 vs 2957 vs 2857 vs/rvs(C-H); CH); CH); vs(C-H); CH)2886 w-2857 vs/r 2643 w2857 vs 2643 w2870 ms2757 sh 2643 w2728 vs2643 w 2571 w2571 w 2571 w-2643 w 2671 w2571 w 2571 w-1620 vs1664 ms1861 ms1618 s1614 vs 1529 v1670 ms1664 ms1861 ms1618 s1614 vs 1529 vvs(C-0) + v(C-C)1520 w1630 vs1432 vs1485 vs1614 vs 1618 sv(C-0) + v(C-C)1520 m1529 m1269 vs1428 vs1400 ss((-1), s((-1), s((-1), s(-1)))1488 m1368 s1432 ms1386 sv(N0,); PA1344 s1263 vs1428 vs1400 ss((-1), s((-1), s((-1)))1344 s1263 vs1312 vs132 vs1428 vs1428 vs1344 s1263 vs1300 vs1342 wIn-plane bending1269 vs1312 w1263 w1314 s1263 vs1424 sv1269 vs1171 s1217 vs1171 s1264 vs1086 s1171 s1171 s1265 s1168 w900 ms865 s4romatic rings vibrations1054 s1014 w1005 s77 s127 vs72 sv72 sw72 sw1054 s1014 s1014 s1055 s100 s77 s129 vs72 sw	5010111		2072 11		3057 w	
2940 mw2914 wv2920 vw ν_{x} (C-H); CH32898 w2857 vs.br2857 vs.br2857 vs.br2857 vs.br2898 w2857 vs.br2857 vs.br2814 vw2856 w2728 vs2728 vsHydrogen bonding-2643 vs2657 vs.br2571 vs2671 w2571 w2571 vs2543 vs1870 ms1664 ms1681 ms1618 s1614 vsOvertone of &(CH)1625 vs1632 vs1632 vs1528 sv(C=0) + v(C=C)1574 s1630 vs1529 vs1282 sv(C=0) + v(C=C)1580 m1529 vs1282 vs1486 vs(MNs)1489 m1529 vs1343 ms1386 s1386 sv(No2); PA1384 s1368 s1312 w1300 vs1387 sv(C-C) + v(C-N) + v(C-O)1295 s1263 vs1343 ms1386 s1385 sv(No2); PA1294 s1207 w1312 w1300 vs1342 win-plane bending1295 s1263 vs1263 vs1214 sin-plane bending1295 s1106 s1143 vs1114 sin-plane bending1295 s1108 s1143 vs1114 s1594 s180 s851 vs829 w900 ms868 s984 s851 vs292 w900 ms828 sAromatic rings vibrations985 s981 vs917 vs728 w714 sy985 s981 vs973 s643 vs686 vsAromatic rings vibrations of ortho substituted985 s599	2982 ms	-	-	2957 vw	2986 vw	$\nu_{\rm s}$ (C–H); CH ₃
2898 w 2857 vs,br 2857 vs,br 2814 vv 2856 w 2814 vv 2814 vv 2856 vs 2814 vv 2828 vv 2857 vs 2814 vv 2814 vv 2857 vs 2814 vv 2817 vv 2864 vv 2857 vv 2814 vv 287 vv 2814 vv 2857 vv 287 vv 2814 vv 2857 vv 287 vv 2814 vv 2814 vv 1870 ms 1664 ms 1861 ms 1618 s 1638 vs 1618 s 1614 vs 0vertone of å(CH) 1528 v 1630 vs 1608 vs 1528 s (C=O) + v(C=C) 1520 v 1529 vs 1428 vv 1400 s δa(CH ₃) + δa(CH ₃) 1488 m 1265 vs 1343 ms 1386 s vu(NO ₂): PA 1321 s 1263 vs 1312 w 1300 vs 1357 s v((NO ₂): PA 1295 s 1168 w 1263 vs 1171 s 1214 s 1286 s 1269 vs 1150 ms 1214 s 128 s Aromatic rings vib	2940 mw			2914 vw	2929 vw	$\nu_{as}(C-H); CH_3$
2856 w 2814 vw - 267 375 sh 2728 vw Hydrogen bonding 2671 w 2571 w 2571 w 2571 w 2870 ms 1664 ms 1861 ms 1618 s 1614 vs Overtone of $\delta(CH)$ 1870 ms 1664 ms 1861 ms 1618 s 1614 vs Overtone of $\delta(CH)$ 1870 ms 1664 ms 1861 ms 1618 s 1557 s v _a (NO ₂): PA 1574 s 1630 vs 1630 vs 1485 vs 1557 s v _a (NO ₂): PA 1570 w 1630 vs 1630 vs 1485 vs 1557 s v _a (NO ₂): PA 1520 w 1630 vs 1630 vs 1485 vs 1568 s v _a (NO ₂): PA 1520 w 1630 vs 1329 vs 1386 s 1386 s v _a (NO ₂): PA 1384 s 1368 s 1386 s 1386 s v _a (NO ₂): PA 1384 s 168 s 1386 s 1386 s v _a (NO ₂): PA 1321 s 168 s 1386 s 1386 s v _a (NO ₂): PA 1295 s 1168 w 1367 w 1386 s 1366 s 1269 vs 1150 ms 1214 s 1217 vs 1055 s 1143 vs 1143 s 1145 s 1039 s 151 vs 818 s <	2898 w			2857 vs,br	2857 vw	
- - 275 γh 278 γw Hydrogen bonding 2643 w 2657 vw 2657 vw 2571 w 2571 w 2571 w 1870 ms 1664 ms 1861 ms 1618 s 1614 vs Overtone of δ(CH) 1652 vs 1630 vs 1632 vs 1485 vs 1557 s vas(N02): PA 1574 s 1520 v 1528 s ((C=)) + ν(C=C) maintain bands 1549 m 1529 v 1485 vs 1368 s 1432 s 1480 v vas(N02): PA 1489 m 1520 v 1263 vs 1343 ms 1368 s 1343 ms 1366 s vas(CH ₃) + λ(C-C) 1384 s 1263 vs 1343 ms 1380 vs 1357 vs v(C-C) + ν(C-N) + ν(C-O) 1295 s 1207 w 1312 w 1300 vs 1328 s 1mplane bending 1295 v 1638 vs 1638 s 1214 s 1214 s 1mot 1154 vs 1432 vs 1043 s 1114 s 1mot 1mot 1055 s 917 vs 928 s 868 s Aromatic rings	2856 w				2814 vw	
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583 s 543 vs 528 s 525 s 443 vs 428 s 425 s 425 s	609 s		522 ms	586 vs	586 w	
525 s 443 vs 428 s 425 s	583 s			543 vs	528 s	
425 s	525 s			443 vs	428 s	
	425 s					

^a s, strong; w, weak; m, medium; sh, shoulder; v, very; br, broad.

^b ν , stretching; δ , bending.



Fig. 4. (a) Infrared spectrum of [(o-TOL)(CA)] CT complex. (b) Infrared spectrum of [(o-TOL)(PA)] CT complex.

and shifted to lower wavenumbers and consequently the intensity was distorted, this results can be summarized as the following explanatory equation;

 $1625 \text{ vs} + 1574 \text{ s} (\text{o-TOL free donor}) \rightarrow$ 1618 s + 1485 vs (o-TOL/CA complex)1614 vs + 1557 s (o-TOL/PA complex)

As expected, the bands characteristic for the o-TOL unit in [(o-TOL)(CA)] and [(o-TOL)(PA)] CT-complexes are existed with small changes in band intensities and frequency values. This could be attributed to the expected symmetry and electronic structure changes upon the formation of the CT-complexes.

3.3. 3.3. ¹H NMR, ¹³C NMR and ¹H–¹H-Cosy spectral studies

The reaction between chloranilic acid and o-tolidine in methanol carried out in 2:1 ratio through formation of hydrogen bond between –OH of CA and –NH₂ group of o-TOL. The ¹H and ¹³C NMR spectroscopic data (Figs. 5 and 6) proved the formation of symmetrical compound with 6 types of hydrogen protons, five on o-TOL molecule and one for the OH of CA, also, the ¹³C NMR spectrum (Fig. 6) for the same product showed signals for 10 different carbons 7 for o-TOL molecule and 3 for CA, this means that, presence of axis of symmetry for the formed product (Formula II).





The full analysis recorded is, ¹H NMR (Fig. 5) (CDCl₃) for symmetrical 2,2'-[(3,3'-dimethylbiphenyl-4,4'-diyl)bis(aminohydroxy)]bis(3,6-dichloro-5-hydroxy-benzo-1,4-quinone), gave a signals at:

δ = 1.25 (br, 2H, 2OH), 1.57 (br, 2H, NH₂), 2.22 (s, 3H, CH₃), 6.73 (d, 1H_b, *J* = 7.5 Hz, Ar–H), 7.24 (d, 1H_c, *J* = 7.5 Hz, Ar–H), 7.26 (s, 1H_a, Ar–H). ¹H–¹H-Cosy indicates (Fig. 7) that H_c coupled with H_b as ortho coupling as shown in spectrum. ¹³C NMR (CDCl₃); δ = 17.6 (CH₃), 115.3, 122.5, 125.0, 128.6, 128.8, 130.9, 132.1, 134.2 and 143.1 (Ar–C and C=O).

On the other hand, the reaction between picric acid and o-TOL in methanol formed an ionic compound on the bases of hydrogen transfer from picric acid –OH to –NH₂ of o-TOL also in ratio 2:1 PA-to-o-TOL. The spectral studies for ¹H, ¹³CNMR (Figs. 8 and 9) proved formation of symmetrical compound between electron rich molecule, o-TOL, and electron deficient, picric acid.



Fig. 9. ¹³C NMR spectrum of [(o-TOL)(PA)] CT complex.







The full analysis recorded is, ${}^{1}H$ NMR (CDCl₃) for symmetrical 3,3'-dimethylbiphenyl-4,4'-diaminium di(2,4,6-trinitrophenolate), gave a signals at:

δ = 2.87 (s, 3H, CH₃), 5.42 (br, 3H, NH₃⁺), 8.56 (d, 1H_b, *J* = 7.8 Hz, Ar-H), 8.91 (d, 1H_c, *J* = 7.8 Hz, Ar-H), 8.89 (s, 1H_a, Ar-H), 10.5 (s, 2H, Ar-H, picrate).

3.4. Thermogravimetric studies

The thermo gravimetric analysis give an idea about the thermal stabilities of the prepared charge transfer complexes and also show the different in physical behavior between the starting and resulting compounds. TG curves of o-tolidine CT complexes are shown in Fig. 10. The o-TOL donor beginning decomposed at ~129 °C with maximum decomposition at 244 °C. The thermal decomposition of o-TOL occurs sum in one step which was detected at 244 °C within the range of 200–800 °C corresponding to loss of $C_{12}H_{16}N_2$ organic moiety representing a weight loss of obs = 88.65%, calc = 88.70% then leaving residual carbon as final product.

TG curve of [(o-TOL)(CA)] CT-complex was thermally decomposed in nearly two decomposition steps within the temperature rang 25-800 °C. The first decomposition step (obs=27.00%, calc=27.92%) within the temperature range 25-288 °C, may be assigned to the liberation of $2Cl_2 + H_2O + 0.5O_2$ molecules. The

Complex	n	Parameter							
		$E(J \operatorname{mol}^{-1})$	Z (s ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔH (J mol ⁻¹)	ΔG (J mol ⁻¹)	r		
[(o-TOL)(CA)]									
CR	1	157	2.62×10^{13}	-7.45	152	148	0.9882		
HM	1	75.6	4.31×10^5	-1.42	71.4	144	0.9975		
[(o-TOL)(PA)]									
CR	1	182	$4.5 imes 10^{16}$	-169.2	178	141	0.9979		
HM	1	129	2.78×10^{5}	-241	125	151	0.9990		

Kinetic parameters of [(o-TOL)(CA)] and [(o-TOL)(PA)] CT-complexes.

n = number of decomposition steps.



Fig. 11. Kinetic curves of decomposition steps of [(o-TOL)(CA)] complex using Coats and Redfern (CR) and Horowitz and Metzger equations.

second decomposition step found within the temperature range 288–800 °C (obs = 22.00%, calc = 22.52%) which are assigned by the removal of $6H_2O$ and $2NH_3$ molecules with remaining a many carbon atoms as a final residual.

The [(o-TOL)(PA)] CT complex was decomposed thermally in two definite decomposition steps (250 and 516 °C) within the temperature rang 100–800 °C. The first decomposition step (obs = 36.50%, calc = 36.55%) within the temperature range 100–395 °C, may be attributed to the liberation of one molecule of PA and NH₂ group from o-TOL donor. The second decomposition step existed within the temperature range 395–800 °C (obs = 63.50%, calc = 63.45%), which are reasonably by the loss of one molecule of PA and C₁₄H₁₄N organic moiety remnant from o-TOL molecule.

3.5. Kinetic thermodynamic studies

The kinetic studies on thermal process are expected to provide sufficient information regarding Arrhenius parameters *viz*. activa-



Fig. 12. Kinetic curves of decomposition steps of [(o-TOL)(PA)] complex using Coats and Redfern (CR) and Horowitz and Metzger equations.

tion energy (E^*) , frequency factor (A), enthalpy of activation (H^*) , entropy of activation (S^*) , free energy of activation (G^*) . From TG data employing Coats–Redfern [32] and Horowitz and Metzger [33] equations various kinetic thermodynamic parameters have been calculated. The kinetic data obtained for the non isothermal decomposition of complexes are given in Table 3 and Figs. 11 and 12. Generally, the value of (A) increases with decrease in E^* and higher value of activation energy suggests the higher thermal stability.

i Coats-Redfern equation is as follows:

$$\operatorname{Ln}\left[\frac{-\ln(1-a)}{T^2}\right] = -\frac{E^*}{RT} + \ln\left[\frac{AR}{\varphi E^*}\right]$$
(8)

where α is the fraction of the sample decomposed at time *T*, where *T* is the derivative peak temperature, *A* is frequency factor, *R* is the gas constant, *E*^{*} is the activation energy and φ is the linear heating rate. A plot of left side vs 1/T gives a slope for the evaluation of activation energy.

ii Horowitz-Metzger equation is as follows:

$$\log\left[\log\frac{w_{\alpha}}{w_{\gamma}}\right] = \frac{E^*\theta}{2.303RT_s^2} - \log 2.303 \tag{9}$$

where $\theta = T - T_s$, $w_{\gamma} = w_{\alpha} - w$, $w_{\alpha} = \text{mass}$ loss at the completion of the reaction; w = mass loss up to time t. The plot of $\log[\log(w_{\alpha}/w_{\gamma})]$ vs θ was drawn and found to be linear from the slope of which E^* was calculated.

The entropy of activation, ΔS^* , was calculated from the following equations. The enthalpy activation, ΔH^* , and Gibbs free energy, ΔG^* were calculated from;

$$\Delta H^* = E^* - RT \tag{10}$$

and
$$\Delta G^* = DH^* - T\Delta S^*$$
 (11)

The higher values of E^* and lower values of (A) favor the reaction to proceed slower than normal [34]. The activation energy values (E^*) of CT-complexes arranged with order of thermal stability as: [(o-TOL)(PA)] > [(o-TOL)(CA)].

From the kinetic and thermodynamic data resulted from the TGA curves and tabulated in Table 3, the following outcome can be discussed as follows:

- 1 The higher values of activation energies of the o-TOL complexes led to thermal stability of the studied complexes.
- 2 The correlation coefficients of the Arrhenius plots of the thermal decomposition steps were found to lie in the range 0.98–0.99, showing a good fit with linear function.
- 3 It is clear that the thermal decomposition process of all o-TOL complexes is non-spontaneous, i.e., the complexes are thermally stable.

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