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Investigation of charge transfer complexes formed between 3,3′-dimethylbenzidine (*o*-toluidine) donor and DDQ, *p*-chloranil and TCNQ as π-acceptors

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Charge-transfer (CT) complex of *o*-toluidine (*o*-tol) with the π-acceptor tetrachloro-*p*-benzoquinone (*p*-chloranil; CHL) has been synthesized and characterized, along with the products of the elimination reaction of *o*-toluidine (*o*-tol) with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and 7,7,8,8-tetracyanoquinodimethane (TCNQ). Their properties and structures have been investigated using electronic absorption and IR spectroscopy as well as elemental analyses of the isolated compounds. The *o*-tol/*p*-CHL CT complex is shown to consist of a CHL^- radical anion and *o*-tol^+ radical cation. The formations of all three compounds result in the appearance of new UV-Vis spectral bands that peaked in intensity at a stoichiometric ratio of 1∶1. ^{1}H-NMR and mass spectra were used to confirm the formation of the *o*-tol/DDQ and *o*-tol/TCNQ products. The new 7,8-dicyano-7′,8′-*o*-toluidilequinodimethane and 2,3-dichloro-5-cyano-6-*o*-toluidil-*p*-benzoquinone products resulted from the rapid reaction of *o*-tol with TCNQ and DDQ, respectively. Thermogravimetric studies showed that the CT-complex decomposes in three steps whereas the new compounds decompose in a single step. Thermodynamic parameters were computed from the thermal decomposition data.

spectroscopic, structural studies, charge transfer complexes, *o*-toluidine, π-acceptors

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A surprising number of biochemical reactions, such as the solubilization of riboflavin by tryptophan [1] or the synergism between vitamin B12 and amino acids in the treatment of megaloblastic anemia [2], are charge transfer (CT) in nature. This type of reaction has been widely studied and reported [3]. Coleman et al. [4] and Ferraris et al. [5] studied the electrical conductivity of the (tetrathia-fulvalene (TTF)/7,7,8,8-tetracyanoquinodimethane (TCNQ) system, and showed that these CT complexes behave like "organic metals", and have significant technological potential. Other notable applications of charge transfer complexes [6–9] included the detection of drugs using spectrophotometry based on the appearance of colored complexes formed by the interactions between (π or σ) electron acceptors and using the drugs as donors. Other notable applications of charge transfer complexes [6–9] included the detection of drugs using spectrophotometry based on the appearance of colored complexes formed by the interactions between (π or σ) electron acceptors and using the drugs as donors. Mulliken [10,11] described charge-transfer interactions within a molecular complex formed from an electron donor (D) and electron acceptor (A) as a resonance with a transfer of charge from D to A to form a radical cation and anion, respectively: $D+A \rightleftharpoons D^+, A^-$. In our previous work [12,13], we discussed the CT complexes of aromatic amines using *o*-toluidine and *p*-toluidine as a donors. In this paper, we advance our study of the interactions between *o*-toluidine and π-acceptors (CHL, DDQ and TCNQ) in chloroform.

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1 Experimental

The reactants; *o*-toluidine, 7,7,8,8-tetracyanoquinodimethane (TCNQ) and tetrachloro-*p*-benzoquinone (*p*-chloranil) were obtained from Merck Company (Germany) and used without further purification. 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was obtained from Aldrich company (USA) and was further purified by re-crystallization from CH_2Cl_2 prior to use. The electronic absorption spectra were recorded on a Jenway 6405 (Bibby Scientific Limited, Beacon Road, Stone, Staffordshire ST15 0SA, UK) with quartz cell with a 1.0 cm path length from 700 to 200 nm. A Genesis II FT IR spectrophotometer (Mattson instruments, USA) was used to take the IR spectra of the reactants and the CT-complexes as KBr discs. ^{1}HNMR spectra of *o*-toluidine/DDQ complex were obtained on a Varian spectrophotometer Gemini 200 MHz (Agilent Technologies, Inc. USA) using TMS as internal reference and d_6-DMSO as the solvent. The mass spectrum of 7,8-dicyano-7′,8′-*o*-toluidilequinodimethane was recorded at 70 eV using an *AEI* MS 30 mass spectrometer (USA). Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were carried out from 25 to 600°C under a nitrogen atmosphere on a Shimadzu TGA 50H thermal analyzer (Japan). A weighed amount was placed in an aluminum crucible under a 30 mL/min flow of nitrogen heated at 15°C/min. The elemental analyses were performed by the microanalysis unit at Cairo University, Egypt, using a Perkin Elmer CHN 2400 (USA). The elemental analysis data (CHN) of the reaction products (CT-complexes) matched the molar ratio gained from photometric titrations. Photometric titrations at 351, 294 and 408 nm were performed for the reactions of *o*-toluidine with DDQ, *p*-chloranil and TCNQ, respectively, using the Jenway 6405 spectrophotometer as follows: A 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50 or 3.00 mL aliquot of a standard solution (5.0×10^{-4} mol/L) of the appropriate acceptor (DDQ, *p*-chloranil and TCNQ) in chloroform was added to 1.00 mL of 5.0×10^{-4} mol/L *o*-toluidine also in chloroform. The total volume of the mixture was hen made up to 5 mL. The concentration of *o*-toluidine (C^o_D) in the reaction mixture was thus fixed at 1.0×10^{-4} mol/L while the concentration of π-acceptors (C^o_A) varied from 0.25×10^{-4} to 3.00×10^{-4} mol/L. These concentrations produce donor∶acceptor ratios from 4∶1 to 1∶3. The absorbance of each CT complexes was measured and plotted as a function with the ratio of (C^o_D)∶(C^o_A) according to a known method [14]. Solid samples of the 1∶1 CT complexes of *o*-toluidine were prepared by mixing chloroform solutions of *o*-toluidine (1.0 mmol) and either DDQ, *p*-chloranil or TCNQ (1.0 mmol). The solutions of CT complexes were kept at room temperature for 8–10 h. The separated solid CT complexes were filtered and washed several times with a minimum amount of methanol and then dried under vacuum over anhydrous $CaCl_2$. The analytical data for the synthesized CT complexes (C, H and N), along with some of their physical properties, are listed in Table 1.

2 Results and discussion

2.1 Electronic spectra

The electronic absorption spectrum of the *o*-toluidine CT complex in $CHCl_3$ is shown in Figure 1 (A). The two new compounds are shown in Figure 1 (B) and (C). New absorption bands are clearly evident. Neither the free donor (*o*-toluidine) nor acceptors (DDQ, *p*-chloranil and TCNQ) have any measurable absorption in these regions. These bands are observed at 294 nm for the complex [(*o*-toluidine)(*p*-chloranil)] and at 351 and 408 for the new [(*o*-toluidine)(DDQ)] and [(*o*-toluidine)(TCNQ)] compounds, respectively. Photometric titrations on these bands show that the both types of reaction are complete at a 1∶1 molar ratio. When dilute, [(*o*-toluidine)(DDQ)] and [(*o*-toluidine)(TCNQ)] compounds are olive green and blue, respectively, but are dark green and dark violet when isolated in the solid state.

The 1∶1 modified Benesi-Hildebrand eq. (1) [15] was used to calculate the values of the equilibrium constant, K (L mol^{-1}) and the extinction coefficient, ε (L mol^{-1} cm^{-1}), for the *o*-toluidine-acceptors (DDQ, *p*-chloranil) CT complexes.

$$C^o_A C^o_D l/A = 1/K\varepsilon + (C^o_A + C^o_D)/\varepsilon, \quad (1)$$

where C^o_A and C^o_D are the initial concentrations of acceptors and *o*-toluidine donor, respectively, while A is the absorbance of the CT band. Plotting the values of $C^o_A C^o_D l/A$ against $(C^o_A+C^o_D)$, gives a straight line with a slope of $1/\varepsilon$ and an intercept of $1/K\varepsilon$ as shown in Figure 2. The values of (ε) and (K) for the three CT complexes, are listed in Table 2.

The energy of each of the CT complexes (E_{CT}) was calculated using the following eq. (2) [16]:

$$E_{CT} = 1243.667/\lambda_{CT}, \quad (2)$$

where λ_{CT} is the wavelength of the CT band of the complex. The E_{CT} values were calculated from eq. (2) and are listed in Table 2.

Generally, these complexes have a high formation constant and extinction coefficient. These high values of K con-

Table 1 Micro analytical data, colour and melting points for the solid molecular complexes of *o*-toluidine with DDQ, CHL and TCNQ

Complex	Colour	Melting point	Calculated (found)		
			%C	%H	%N
o-tol-DDQ	Dark green	288–290	61.17 (61.07)	3.64 (3.62)	10.19 (9.98)
o-tol-chl	Dark green	302–305	52.40 (52.31)	3.49 (3.47)	6.11 (6.09)
o-tol-TCNQ	Dark violet	315–317	79.56 (78.93)	4.97 (4.78)	15.47 (15.15)

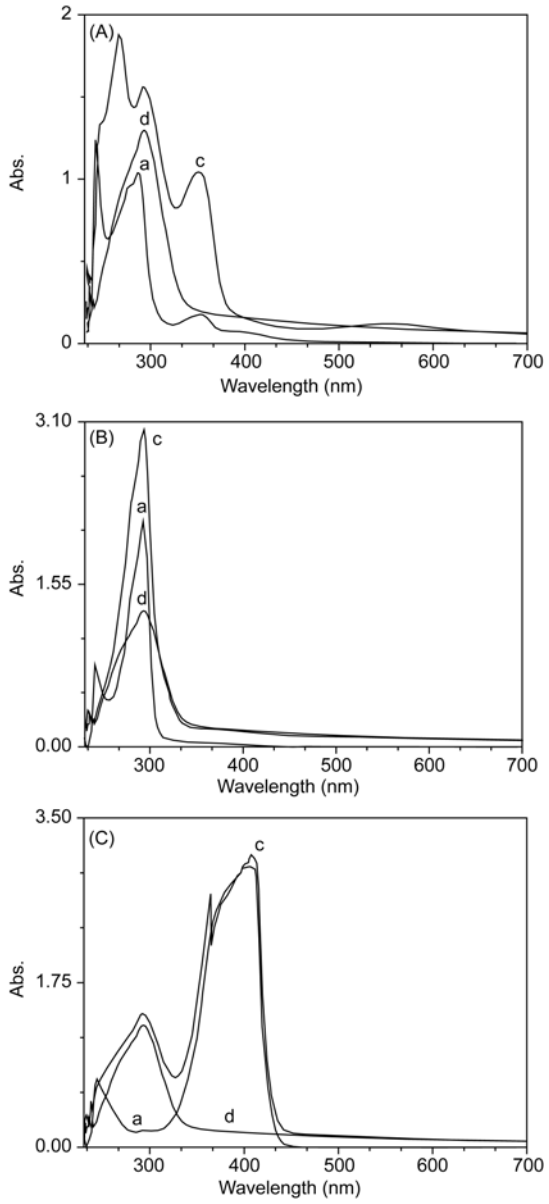


Figure 1 Electronic spectra of the reactions: [(*o*-tol)(DDQ)] (A); [(*o*-tol)(*p*-chl)] (B); and [(*o*-tol)(TCNQ)] (C). The individual traces are: pure donor (d); pure acceptor (a) and the formed CT-complex (c).

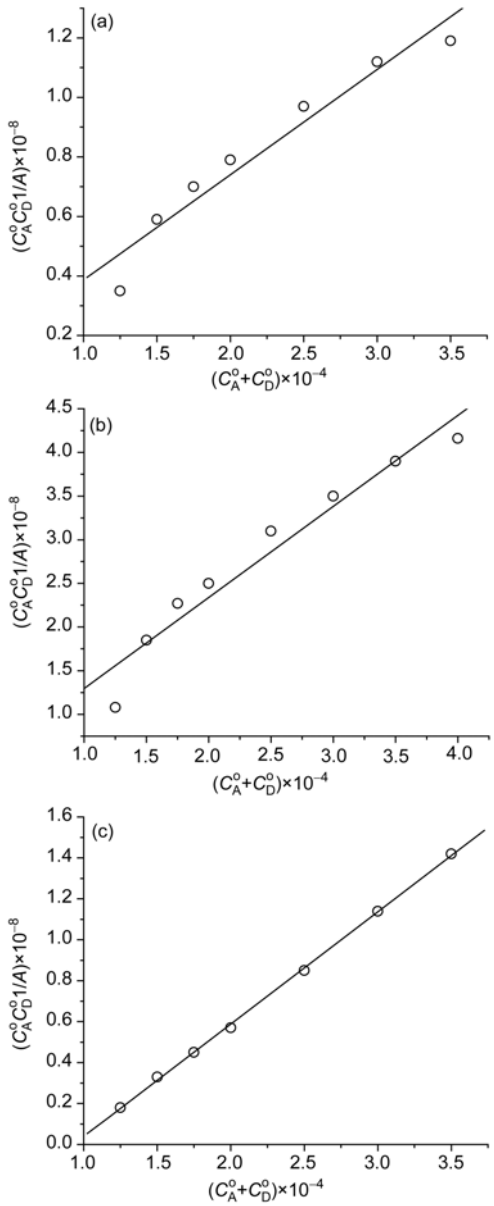


Figure 2 Spectral determination of the association constants and molar extinction coefficients of *o*-tol-DDQ (a), *o*-tol-*p*-chl (b) and *o*-tol-TCNQ (c) systems.

firm the expected high stabilities of the CT-complexes because of the extensive donation from the *o*-toluidine due to the amino and methyl groups. The formation constants also depend on the nature of the acceptor.

2.2 Infrared spectra

IR absorptions similar to the free donor (*o*-toluidine) and π-acceptors (DDQ, *p*-chloranil and TCNQ) were detected in the IR spectra of the CT complexes. These data are represented in Table 3 and shown in Figure 3. The donation process from then *o*-toluidine to the π-acceptors can occur either from the lone pair of electron on the nitrogen atom of

Table 2 Spectroscopic data

Acceptors	λ_{CT} (nm)	E_{CT} (eV)	K_{CT} (mol^{-1})	ε (mol^{-1} cm^{-1})
DDQ	351	3.54	109112	28269
p-chl	294	4.23	41083	9592
TCNQ	408	3.05	10776	18227

amino groups or from the aromatic rings [12,13,17]. The nitrogen atoms have been identified as the donation source in most cases studied. IR spectroscopy has been used to distinguish between the two possibilities. In this case the ν(N–H), ν(C–N) and δ(N–H) bands of *o*-toluidine donor were shifted to lower frequencies on formation of the complex.

Table 3 Infrared frequencies[a] (cm^{-1}) and tentative assignments for characteristic bands of: (**1**) *o*-toluidine, (**2**) *p*-chloranil, (**3**) DDQ, (**4**) TCNQ, (**5**) [(*o*-toluidine)(*p*-chloranil)], (**6**) 2,3-dichloro-5-cyano-6-*o*-toluidil-*p*-benzoquinone and (**7**) 7,8-dicyano-7',8'-*o*-toluidilequinodimethane

Compounds	ν(N–H)	ν(C≡N)	ν(C═O)+ν(C═C)+δ(NH_2)	ν(C–Cl)
1	3475 s 3412 s 3375 s 3338 ms	–	1625 vs 1573 s 1520 w	–
2	–	–	1680 vs, 1583 vs, 1555 sh	819 s 733 s
3	–	2236 ms	1680 vs, 1555 vs	821 s 736 s
4	–	2220 vs	1670 vs, 1539 vs	–
5	3464 m 3407 vw 3359 m	–	1667 s, 1625 vs, 1568 ms 1552 ms, 1490 vs	808 ms 693 s
6	3454 vw 3323 w	2254 w 2219 m	1675 vs, 1651 m, 1615 vw 1557 vs, 1536 sh	803 s 724 s
7	3469 w 3412 m 3370 ms 3249 m	2212 s	1657 m, 1620 s, 1573 ms 1536 w, 1494 m	–

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

The stretching vibration frequencies of ν(C≡N) groups at 2236 (ms) and 2220 (vs) cm^{-1} for the free DDQ and TCNQ acceptors, respectively, moved to 2219 (w) and 2212 (s) cm^{-1} respectively, in their complexes. Further, the group of bands assigned to ν(C–Cl) vibrations, which appeared at about 820 and at 734 cm^{-1} in both free DDQ and *p*-chloranil, exhibited a shift to lower wavenumbers at 803 (s) cm^{-1} and 724(s) cm^{-1}) for the DDQ complex and at 808 (ms) cm^{-1} and 693 (s) cm^{-1} in the *p*-chloranil complex.

The IR spectrum of free *p*-chloranil exhibits a very strong band at 1680 cm^{-1} because of the stretching vibration of ν(C═O), compared to its CT complex. This vibration also moved to lower wavenumbers. The [(*o*-toluidine)(*p*-chloranil)] complex contains the sum of the spectra of the corresponding donor and acceptor. The interaction between the donor *o*-toluidine and *p*-chloranil has two possible transitions; either π-π^* and/or *n*-π^*. Here there is clear evidence for the formation of *p*-chloranil anion radicals; CHL^- as shown in Scheme 1. The conductance of the [(*o*-toluidine)(*p*-chloranil)] CT complex was measured and showed a small increase. This small increase due to complexation shows that the charge transfer complex is present as an ion pair and there are few free ions in solution.

2.3 ^{1}H-NMR spectra

The ^{1}H-NMR spectrum of the 2,3-dichloro-5-cyano-6-*o*-toluidil-*p*-benzoquinone product in DMSO is shown in Figure 4. The three proton singlet at δ 2.513 was assigned to the protons of the two methyl groups (*o*-toluidine) when attached to DDQ. The NH_2 group at 4.76 in the free donor was shifted to δ 4.597, but only contains one proton in the complex. This indicates that one of CN groups of DDQ has been eliminated by the amino group of the *o*-toluidine donor, eliminating HCN (Scheme 2). On the other hand, the second NH_2 group of the free donor has been shifted downfield to 6.380. In the aromatic region, six protons on the two aromatic rings of *o*-toluidine have been split and now appear at δ 6.900, 7.155, 7.411 and 7.999. The intensities and chemical

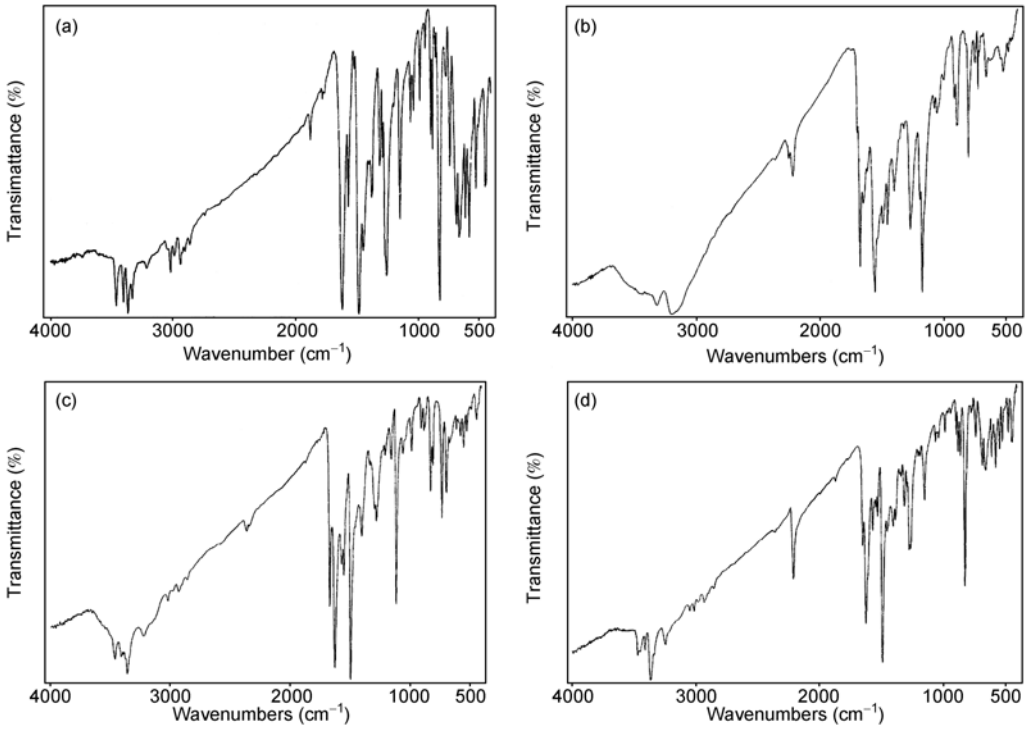
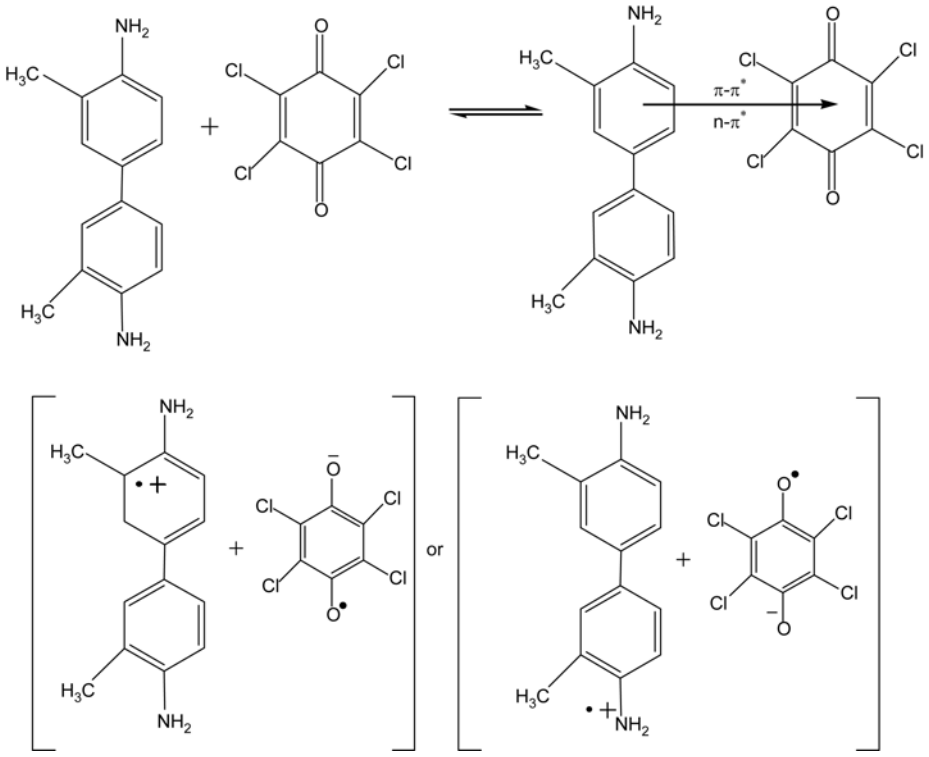


Figure 3 Infrared spectra of compounds *o*-tol (a), [(*o*-tol)(DDQ)] (b), [(*o*-tol)(*p*-chl)] (c) and [(*o*-tol)(TCNQ)] (d).



Scheme 1 The molecular structure of the *o*-toluidine/*p*-chloranil system.

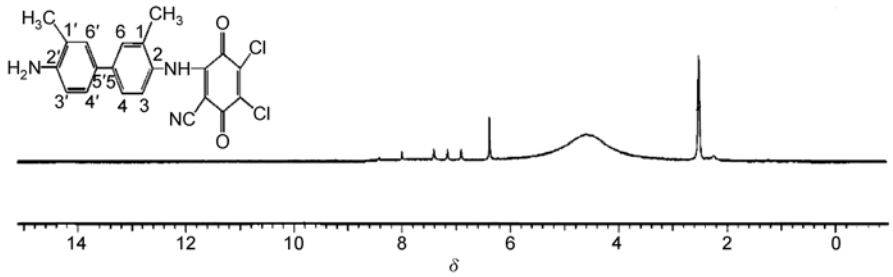
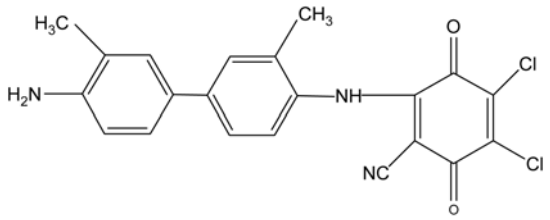


Figure 4 ^{1}H NMR spectra of 2,3-dichloro-5-cyano-6-*o*-toluidil-*p*-benzoquinone.



Scheme 2 2,3-dichloro-5-cyano-6-*o*-toluidil-*p*-benzoquinone.

shifts of the aromatic signals have been significantly affected by the elimination and the accompanying changes in the structured configuration.

2.4 Mass spectra

The mass spectrum (Figure 5) of the new compound 7,8-dicyano-7′,8′-*o*-toluidilequinodimethane (Scheme 3) displayed a molecular ion peak M^{+} at *m/z* (%) 362 (1.49). The following fragments observed in the mass spectrum of the compound confirm the assigned structure of the compound (Scheme 4). The peaks at 313, 264, 226, 200, 135, 87 and 56 were characteristic and assigned to the fragments which correspond to the sequential loss of C_4H, C_4H, C_3, HCN, C_3N_2, C_4 and CH_5N, respectively.

2.5 Thermal analysis

Thermogravimetric analysis (TGA and DTG) was used to gain information about the thermal stabilities of the *o*-toluidine CT complex and new compounds. The main thermogravimetric values for them are given in Table 4 and the kinetic parameters are listed in Table 5.

The two novel organic products, 7,8-dicyano-7′,8′-*o*-toluidilequinodimethane and 2,3-dichloro-5-cyano-6-*o*-toluidil-*p*-benzoquinone were formed by an elimination reaction

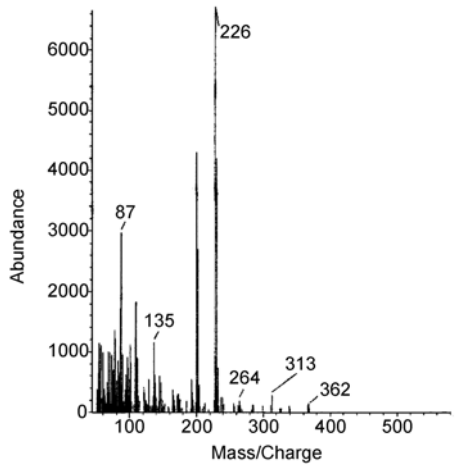
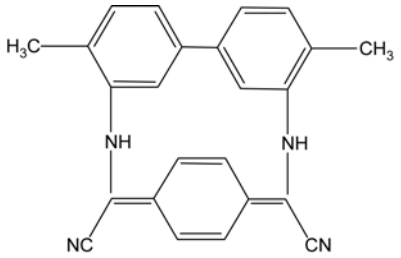
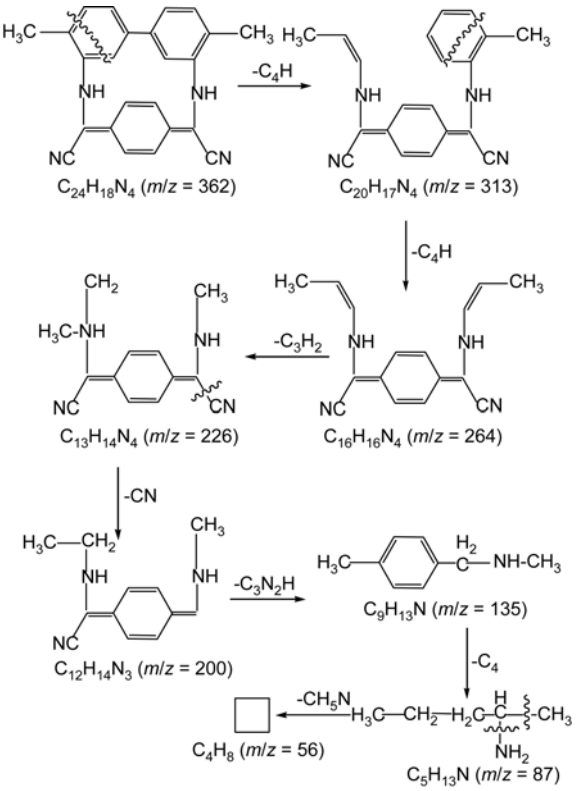


Figure 5 Mass spectra of 7,8-dicyano-7′,8′-*o*-toluidilequinodimethane.



Scheme 3 7,8-dicyano-7′,8′-*o*-toluidilequinodimethane.



Scheme 4 A possible fragmentation process for 7,8-dicyano-7′,8′-*o*-toluidilequinodimethane.

Table 4 Thermogravimetric data of 7,8-dicyano-7′,8′-*o*-toluidilequinodimethane (I), 2,3-dichloro-5-cyano-6-*o*-toluidil-*p*-benzoquinone (II) and [(*o*-toluidine)(*p*-chl)] (III) compounds

Compounds	DrTG max (°C)	TG results			
		T range (°C)	Mass loss (%) Found (Calc.)	Loss	Residue
I	290	100–600	60.01 (60.22)	$2NH_3+6C_2H_2$ N_2	12C
II	219	100–600	64.47 (65.05)	$NH_3+4C_2H_2$ $N_2+2HCl+CO_2+H_2$	12C
III	166 236 376 579	40–600	61.17 (60.70)	$2C_2H_4+2NH_4Cl+$ CO_2+Cl_2	15C

Table 5 Kinetic parameters data of 7,8-dicyano-7′,8′-*o*-toluidilequinodimethane (I), 2,3-dichloro-5-cyano-6-*o*-toluidil-*p*-benzoquinone (II) and [(*o*-toluidine)(*p*-chl)] (III) compounds

Compounds	Parameter					*r*
	E (kJ mol^{-1})	*Z* (s^{-1})	ΔS (J mol^{-1} K^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	
I	30.80	1.09×10^5	–153	26.50	106	0.9746
II	72.30	2.99×10^5	–144	68.30	139	0.9959
III	98.90	1.26×10^8	–94.3	–94.70	143	0.9975

between *o*-toluidine with TCNQ and DDQ, respectively. The thermal diagrams (Figure 6 (a) and (b)) of *o*-toluidine/TCNQ and *o*-toluidine/DDQ compounds show only one decomposition step within the temperature range which 100–600°C corresponds to the loss of $2NH_3+6C_2H_2+N_2$ at 290°C and a mass loss of 60.01% for *o*-toluidine/TCNQ system and loss of $NH_3+4C_2H_2+N_2+2HCl+H_2+CO_2$ at 219°C for *o*-toluidine/DDQ system with a mass loss of 64.47%. Both are in good agreement with the calculated mass loss values of 60.22% and 65.05%, respectively.

The [(*o*-toluidine)(*p*-chloranil)] CT complex however exhibited a four step decomposition process over 40–600°C. The four decomposition steps which occurs at 166, 236, 376 and 579°C which has been assigned to the loss of $2C_2H_4+2NH_4Cl+CO_2+Cl_2$ giving an overall mass loss of 61.17% (calcd. 60.70%).

2.6 Kinetic data

The kinetic parameters for the decomposition of the compounds namely, activation energy (E^*), enthalpy (ΔH^*), entropy (ΔS^*) and free energy of the decomposition (ΔG^*) as well as the pre-exponential factors (A) were evaluated graphically (Figure 7) using the Coats-Redfern [18] relationship:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]=\ln\left(\frac{ZR}{\varphi E}\right)-\frac{E}{RT},$$

where α and φ are the fraction of the sample decomposed at time t and the linear heating rate, respectively. R is the gas

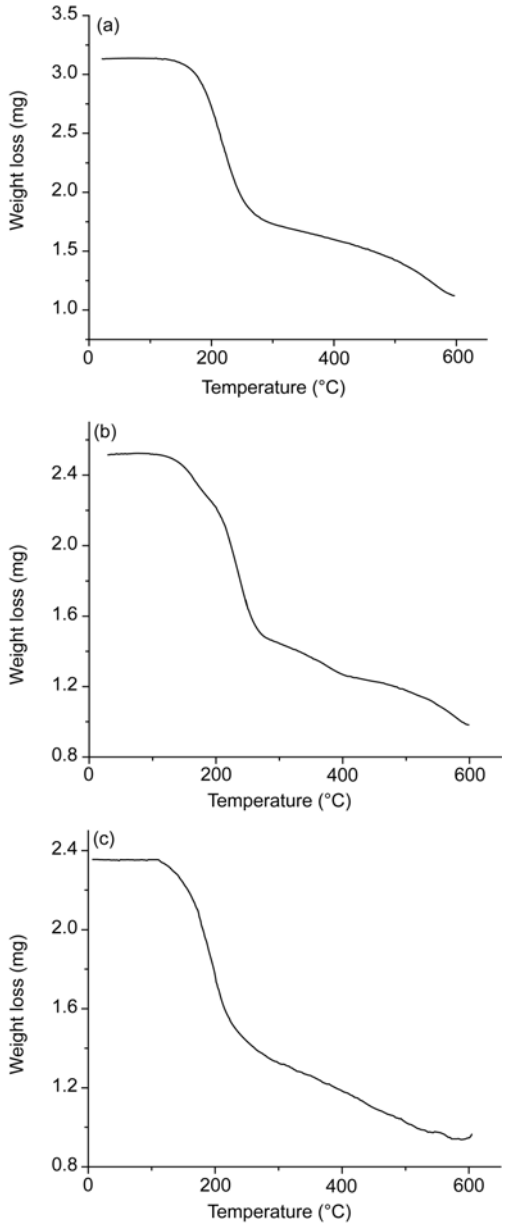


Figure 6 TGA diagrams of [(*o*-tol)(DDQ)] (a), [(*o*-tol)(*p*-chl)] (b) and [(*o*-tol)(TCNQ)] (c).

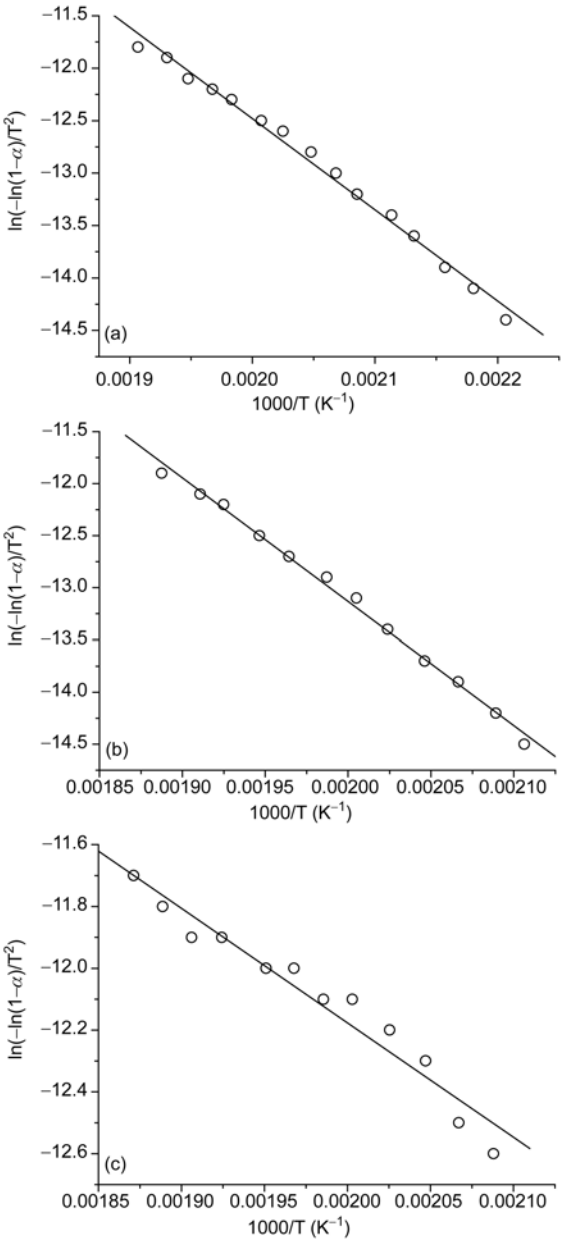


Figure 7 Kinetic diagrams of [(*o*-tol)(DDQ)] (a), [(*o*-tol)(*p*-chl)] (b) and [(*o*-tol)(TCNQ)] (c).

constant and E is the activation energy in kJ mol^{-1}. A plot of $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ against $1/T$ gives a slope from which E^* was calculated and Z (Arrhenius constant) was determined from the intercept. The entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and the free energy change of activation (ΔG^*) were calculated using the following eqs.

$$\Delta H = E - RT_m, \quad \Delta G = \Delta H - T_m \Delta \mathrm{S},$$

where T_m is the DTG peak temperature. The calculated values of E^*, Z, ΔS^*, ΔH^* and ΔG^* for the decomposition steps are given in Table 5. Comparing the activation energy of the initial decomposition for all the compounds gave the order CHL>DDQ>TCNQ for the different acceptors. This difference may be caused by the reactivity of the complexes and the electronic configuration of the acceptor when attached to *o*-toluidine. These results agree well with those of the TG analysis discussed above. ΔS^* values of the main stage for all complexes were found to be negative which indicates that the activated complex was more ordered than the reactants.

3 Conclusion

The interactions between the electron donor *o*-toluidine and

the acceptors 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) were studied spectrophotometrically in chloroform. A new charge-transfer complex was isolated and characterized through elemental analysis, (infrared, HNMR, electronic, and mass spectra) as well as thermal and kinetic thermodynamic studies along with two new products. The stoichiometry of the products was found to be 1∶1 in all cases. Accordingly, the formed CT-complex/compounds have the formulas [(*o*-tol)(chloranil)], [(*o*-tol)(DDQ)], and [(*o*-tol)(TCNQ)].

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