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Synthesis, spectroscopic and computational studies on charge-transfer complexes of 1,4-benzoquinone

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ABSTRACT

Treatment of 1,4-benzoquinone as acceptor with aniline, 2-tolidine, 4-toluidine, 2-aminothiazol and 8-hydroxylquinoline as donors gave charge transfer complexes in good yields. The complexes were characterized by elemental analyses, IR and $^1\text{H-NMR}$ spectroscopy. The data obtained indicate the formation of 1:1 charge transfer complexes, also a charge transfer interaction associated by intermolecular hydrogen bonding ($n-\pi^*$ electronic). The normal $\pi-\pi^*$ electronic interaction take place by transferring an electron from the donors ring to the acceptor ring. The equilibrium constants, the extinction coefficients calculated using equation such as modified Benesi-Hildebrand, The free energy, ionization potential and transition energy of the complexes were calculated.

Keyword: charge transfer complexes, acceptor, donors, the equilibrium constants and the extinction coefficients of the complexes.

INTRODUCTION

The term charge transfer gives a certain type of complex resulting from interactions of donor and acceptor with the formation of weak bond (1,2) and discussed widely by Foster (3). Charge transfer complexes using organic species are intensively studied because of their special type of interaction, which is accompanied by the transfer of an electron from the donor to the acceptor (4,5). In addition, protonation of the donor from acidic acceptors is generally a route for the formation of ion pair adducts (6,7). Electron donor-acceptor complex formation between acceptors and anilines has been studied (8,9). 1,4-Benzoquinone is the parent molecule of a class of compounds which play a relevant role in biological systems and in the formation of charge-transfer salts, most of the organic conductors based on charge-transfer complexes contain a 1,4-benzoquinone derivative as the acceptor component (10,11). Reactions of 1,4-benzoquinone with aromatic amines have been carried out (12,13). The reaction between 2-toluidine and 4-toluidine with 1,4-benzoquinone derivatives have been discussed (14-17). The reactions of 8-hydroxyquinoline with 1,2,3-trihydroxybenzene, nitrophenols and 2,4,5-trichlorophenol in solid state have been studied spectroscopically (18-21). Interaction of 2-aminothiazole base with acceptors give 1:1 molecular species (22,23). Herein, the spectrophotometer studies have been carried out for charge-transfer complexes of 1,4-benzoquinone with aniline, 2-tolidine, 4-toluidine,

2-aminothiazol and 8-hydroxylquinoline in methanol solvent. The equilibrium constant of charge-transfer complex (K_{CT}), molar extinction coefficient of CT complex (ϵ_{CT}), (ΔG°), (I_p) and (ΔE°) were calculated. The synthesized 1,4-benzoquinone CT-complexes were structurally characterized to interpret the behavior of interactions using IR, ^1H NMR, UV-Vis techniques and elemental analyses. HOMO, LUMO and energy gap values of donors and CT-complexes were determined.

MATERIALS AND METHODS

Reagents

The compounds and solvents were purchased from Aldrich Chemical Company. Crystallization of 1,4-benzoquinone from 95% ethanol, (e.g. from room temperature to liquid N₂). It slowly decomposes and should be stored, refrigerated, in an evacuated or sealed glass vessel in the dark. It should be resublimed before use (24).

Instrumentals

Elemental analyses were measured at the Micro analytical unit of the Cairo University. The electronic absorption spectra of solutions of the CT complexes were measured on a Shimadzu UV-spectrophotometer model 1601 PC using 1 cm matched quartz cell. Infrared spectra were recorded on a Perkin-Elmer 683 IR, spectrophotometer in Nujol mull. ¹H NMR spectra of the compounds were recorded using Bruker, 300 MHz NMR spectrometer. ¹H NMR spectra were obtained on a Varian Gemini 200 MHz spectrometer. ¹H NMR data are expressed in parts per million (ppm), referenced internally to the residual proton impurity in DMSO (dimethylsulfoxide, d₆) solvent and the reported of chemical shift (m = multiplet, s = singlet and br = broad).

Computational method

The drawing of the structure of the donors and acceptors were carried out on the Chem-Draw ultra 12.0 software and the structures were transported to Chem3D ultra 12.0 software for optimization.

Methods

Preparation of standard solutions

The electronic spectra of 1,4-benzoquinone (acceptor) with aniline, 2-tolidine, 4-toluidine, 2-aminothiazol and 8-hydroxylquinoline (donors) were measured in methanol as a blank. The CT complexes were formed by adding X ml (X = 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 (1,4-benzoquinone) in methanol was added to 1.00 mL of 5.0×10⁻⁴ mol/L donors also in methanol. The total volume of the mixture was 5 mL. The concentration of donors [D]₀ in the reaction mixture was thus fixed at 1.0×10⁻⁴ mol/L while the concentration of acceptor [A]₀ varied from 0.25×10⁻⁴ to 3.00×10⁻⁴ mol/L. The modified Benesi-Hildebrand method (25) were applied for the determination the formation constant, K_{CT}, and the absorptivity, ε_{CT}, values for each CT-complex resulted from this study.

Computational method

The drawing of the structure of the donors and acceptors were carried out on the Chem-Draw ultra 12.0 software and the structures were transported to Chem3D ultra 12.0 software for optimization.

Synthesis of the charge transfer complex

The solid CT complex was prepared by mixing the saturated solution of 1,4-benzoquinone (0.1081 gm, 1mmol) in 20 ml methanol with saturated solution of aniline(0.0931 gm, 1mmol), 2-tolidine (0.2144 gm, 1mmol), 4-toluidine (0.1072 gm, 1mmol), 2-aminothiazol (0.1001 gm, 1mmol) and 8-hydroxylquinoline (0.1452 gm, 1mmol) in 20 ml methanol. The mixture was stirred at room temperature for 3h. The complexes were recrystallized from methanol. Elemental analyses for all complexes demonstrated the formation of 1:1 molecular species and physical measurements data of CT complexes formed were listed (Table 1).

Table 1. Elemental analysis and Physical parameters data of charge transfer complex

Complex	Color	Formula	(M _w)	mp. °C	Elemental analysis ^a		
					%C	%H	%N
An-Bq	grey	C ₁₂ H ₁₁ NO ₂	(201.23)	140	71.63(71.01)	5.51(5.99)	6.96(7.40)
2-Tol-Bq	brown	C ₁₈ H ₂₀ N ₂ O ₂	(296.37)	236	72.95(72.11)	6.80(6.99)	9.45(9.90)
4-Tol-Bq	black	C ₁₃ H ₁₃ NO ₂	(215.26)	135	72.54(72.98)	6.09 (5.77)	6.51 (6.07)
8-Hq-Bq	brown	C ₁₅ H ₁₁ NO ₃	(253.26)	210	71.14(70.94)	4.38 (4.12)	5.53 (5.78)
2-At-Bq	Deep brown	C ₉ H ₈ N ₂ O ₂ S	(208.24)	290	17.31(17.88)	1.94 (1.77)	13.46 (13.11)

^a Calculated (found)

RESULTS AND DISCUSSION

Infrared spectra

The infrared spectra of the characterized bands of 1,4-benzoquinone (Bq), aniline (An), 2-aminothiazole (2-Ath), 4-toluidine (4-Tol), 2-toluidine (2-Tol) and 8-hydroxylquinoline (8-Hq) are represented in Table 2. The possibility of a donation process between 1,4-benzoquinone and donors (aniline, 2-aminothiazole, 4-toluidine, 2-toluidine) may be caused by a lone pair on the nitrogen atom of the amino group (26).

In Table 2, the spectra of free 1,4-benzoquinone, show a very strong band at 1680 cm^{-1} due to the stretching vibration of $\nu(\text{C}=\text{O})$. The spectra of their separated CT complexes show the following feature: a shift of $\nu(\text{C}=\text{O})$ due to a lower wavenumber is observed. This shift was attributed to the charge transfer from donor to acceptor upon complexation. This happened because of the expected changes in molecular symmetry and electronic structure of the reactants upon complexation. Therefore, CT complexation between aniline and 1,4-benzoquinone is strongly supported by IR spectra. There were changes in intensities of the peaks that distinguish the $-\text{NH}_2$ group (the donation sites for the aniline) (27) and also there were shifting for the peaks. The N-H stretching vibration is observed at 3011 cm^{-1} in spectrum of the CT complex whereas in free aniline this is observed at 3442 cm^{-1} . The Infrared spectrum of 4-toluidine donor exhibits a group of bands at 3420–3330 cm^{-1} , which are assigned to the stretching vibrations $\nu(\text{N-H})$ and 2986, 2852 cm^{-1} (CH_3 str.). In comparison to the CT complex that resulted, it was observed that there is shift in the $\nu(\text{N-H})$ to lower wavenumber values. IR spectra of the characterized bands of 8-hydroxylquinoline, 1,4-benzoquinone and [(8-Hq)(Bq)] were represented in Table 2. The formation of CT complex were associated by hydrogen bonding between one Oxygen atom of Bq and Hydrogen atom of the OH group of 8-Hq (21). The shift of the IR bands of the acceptor to lower wavenumbers and those of the donors part to higher values reflects a donor to acceptor charge transfer of $\pi-\pi^*$ interaction, i.e. $D_{\text{HOMO}} \rightarrow A_{\text{HOMO}}$ transition (28).

Table 2. Infrared frequencies and tentative assignments for acceptor, donors and CT complexes

Compounds	$\nu(\text{N-H})$	$\nu(\text{OH})$	$\nu(\text{C=O})+\nu(\text{C=C})+\delta(\text{NH}_2)$	hydrogen bond
Bq	3442 ms		1680 vs	
			1410 vs	
			1311 ms	
			1220 vs	
An	3442 ms		1619 vs	
	3360 s		1281 m	
	3225 v		764 vs	
2-Tol	3475 s		1625 vs	
	3412 s		1573 s	
	3375 s		1520 w	
4-Tol	3338 ms		1489 vs	
	3417 ms		1625 vs	
	3375 w		1594 sh	
2-At			1777 vw	
	3413 s		1629 s	
	3144 s		1527 s	
	3293 ms		1520 s	
	3122 s		1498 ms	
			1492 ms	
8-Hq			1403 vw	
			1201 ms	
			1031 v	
	3042 s,br		1577 ms	
			1500 vs	
			1473 w	
Bq-An			1376 ms	
			1274 vs	
	3011 m		1606 ms	2006 v
	2909 vw		1469 vs	1941 v
	2836 m		823 vs	1851 v
	2698 m			1782 v
Bq-2-Tol	3242 ms		1629 vs	1978 vw
	3055 vw		1510 vw	1778 vw
			1466 ms	
Bq-4-Tol	3231 m		1629 vs	1978 vw
			1510 vw	1778 vw
			4166 ms	
Bq-8-Hq	3410 s,br		1645 ms	2363 v
			1499 ms	
			1455 w	
			1411 w	
Bq-2-At			1375 w	
	3324 m		1606 ms	2006 v
	3109 vw		1469 vs	1941 v
			823 vs	

Absorption spectra

The electronic spectra of the aniline, 2-toluidine, 4-toluidine, 2-aminothiazole and 8-hydroxyquinoline (An, 2-Tol, 4-Tol, 2-At and 8-Hq) as a donors with 1,4-benzoquinone (Bq) as π -acceptor and their CT complexes are shown in Fig.1A,B,C, D and E. The bands of [(An)(Bq)] are observed at 305 and 295 nm for the complex in Fig 1A and [(2-At)(Bq)] are observed at 270 nm (Fig.1E). also, the spectra in the case of [(2-Tol) (Bq)] system have definite bands at 295 nm (Fig. 1B). The corresponding absorption bands associated with the formation of the complex [(8-Hq)(Bq)] are observed at 310 nm (Fig 1D). All of these CT bands disappeared in the spectra of both the donors and acceptors, it seemed shifted to red or blue wavelengths [(8-Hq)(Bq) or (An)(Bq), (2-At)(Bq) and (2-Tol)(Bq)] which indicate the formation of the charge transfer (29). The electronic spectra of the 4-toluidine (4-Tol) as a donor with 1,4-benzoquinone (Bq) as an acceptor and their CT-complexes are shown in Fig.1C. The spectra of the [(4-Tol)(Bq)] system have definite bands at 287 nm (hyperchromic effect). The change of the absorbance intensity to higher when adding the acceptor to donor was detected and investigated to form CT complex (15). The possibility of a donation from the aniline, 2-toluidine, 4-toluidine and 2-aminothiazole to 1,4-benzoquinone exists by a ion pair of electrons on the nitrogen atom of $-NH_2$ group and the carbonyl oxygen of Bq (30,31). Also, form hydrogen bonding between 8-hydroxy-quinoline and acceptor in the complex (20). The absorption bands were characteristic of an intermolecular charge transfer involving the overlap of the lowest unoccupied molecular orbital (LUMO) of the acceptor with the highest occupied molecular orbital (HOMO) of the donor. The donors are relatively electron rich and Bq is relatively electron poor compound, they tend to associate with one another in a loose interaction known as electron - donor - acceptor (EDA) complexes. The low energy absorptions observed in solutions containing both a donor and an acceptor which have been described by Mulliken (32) as charge transfer transitions involving the excitation of an electron on the donor to an empty orbital on the acceptor.

The formation constant (K_{CT}) and molar extinction coefficients (ϵ_{CT}) were calculated using the following modified Benesi-Hildebrand equation (25). The modified Benesi-Hildebrand analysis of K_{CT} involves the measurement of the D--A CT absorbance (A) as a function of varied $[A]_0$ when $[A]_0 \gg [D]_0$. A plot of $x = [A]_0 + [D]_0$ vs $y = [A]_0 [D]_0 / A$ gives a y-intercept = $1/K_{CT}\epsilon_{CT}$ and slope = $1/\epsilon_{CT}$ (Fig 2, Table 3).

$$[A]_0 [D]_0 / A = [A]_0 + [D]_0 / \epsilon_{CT} + 1/K_{CT}\epsilon_{CT} \quad (1)$$

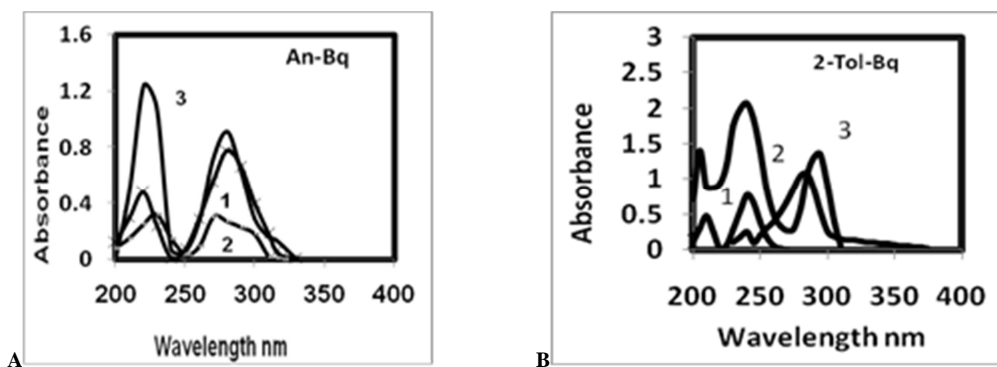
where A = absorbance of the charge transfer band complex,

$[A]_0$ = initial concentration of the electron acceptor,

$[D]_0$ = initial concentration of the electron donor,

K_{CT} = formation constant of charge transfer complex in solution, and

ϵ_{CT} = molar extinction coefficient.



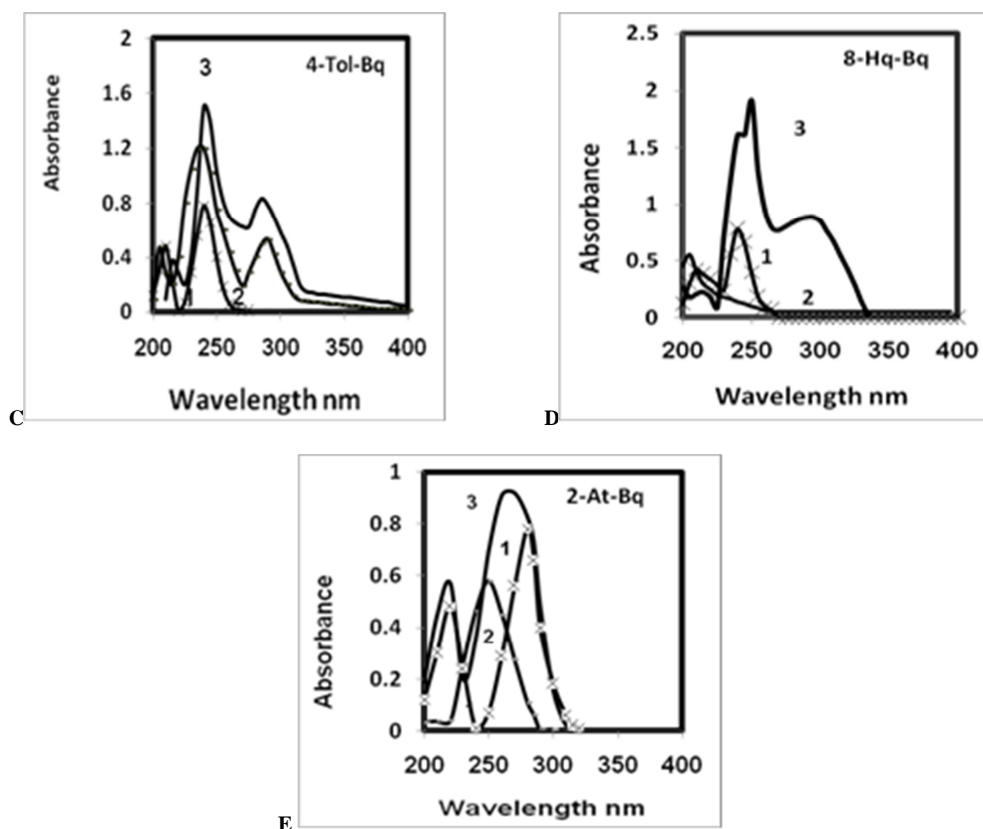


Figure 1. Electronic absorption spectra of A- [(An)(Bq)], B- [(2-Tol)(Bq)], C- [(4-Tol)(Bq)], D- [(8-Hq)(Bq)] and E- [(2-At)(Bq)] where 1- acceptor (1×10^{-4} M), 2- donor (1×10^{-4} M) and 3- CT complex (1×10^{-4} M)

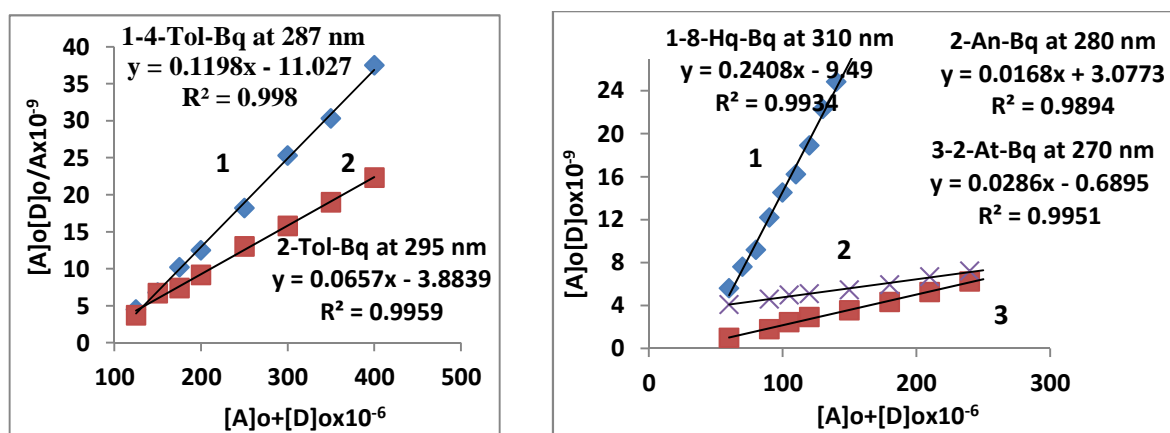


Fig. 2. Relation between $[A]_0[D]_0/A \times 10^9$ and $[A]_0 + [D]_0 \times 10^{-6}$ for the complex of A- 1-[(4-Tol)(Bq)] and 2-[(2-Tol)(Bq)], B- 1-[(8-Hq)(Bq)], 2-[(An)(Bq)] and 3-[(2-At)(Bq)]

The standard free energy of complex was calculated from the formation constant by the following equation (33):

$$\Delta G^\circ = -RT \ln K_{CT} \quad (2)$$

Where ΔG° was the free energy of the complex, R is gas constant, T is the temperature in Kelvin degree and K_{CT} was the formation constant of complex (Table 3). The complex were found to have small value of $-\Delta G^\circ$ value ($K_{CT} > 1, \Delta G^\circ < 1$), indicating a weak nature of the complex and spontaneous reaction between D^+ and A^- .

From the electronic spectra of CT charge transfer compounds calculate the electron energy transition E_{CT} , I_p is ionization potential of donor, E_A is electron affinity of acceptors (Table 3).

Electron energy transition E_{CT} calculated by applying the following equation (34):

$$E_{CT} = 1243.667/\lambda(\text{nm}) \quad (3)$$

The I_p values can be calculated through the use of the following:

$$I_p = a + bv$$

Where a and b are constants amounting to 4.390 and 0.857(35) or 5.156 and 0.778 (36) or 5.110 and 0.701(37). v is transition energy from HOMO to LUMO (π - π^*) transition of the free donor, which is taken approximately for that in solution (the solvation energy is low compared to electronic excitation energy).

E_A is electron affinity of acceptor calculated by using Briegleb relation (7).

$$E_{CT} = I_p - (E_A + C) \quad (4)$$

Where I_p is ionization potential of donor, E_A is electron affinity of acceptor and C is Coulombic force = 5.2 eV(38). Electron affinity of the acceptor can be calculated through a linear relationship between E_{CT} against I_p (Fig. 3) and from intercept can be calculated electronic affinity of p-benzoquinone. In the present work, E_A is equal to 1.93 (39).

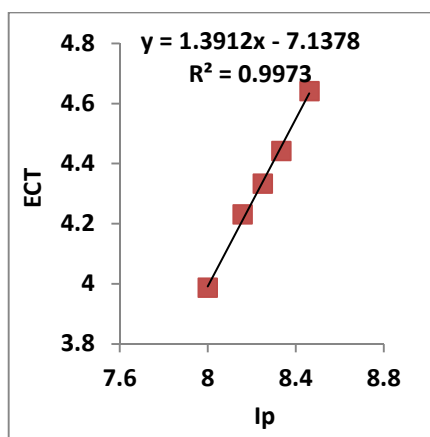


Fig. 3. Plot of CT transition energies of complexes versus ionization potential

Table 3. Physical parameters data of the complex

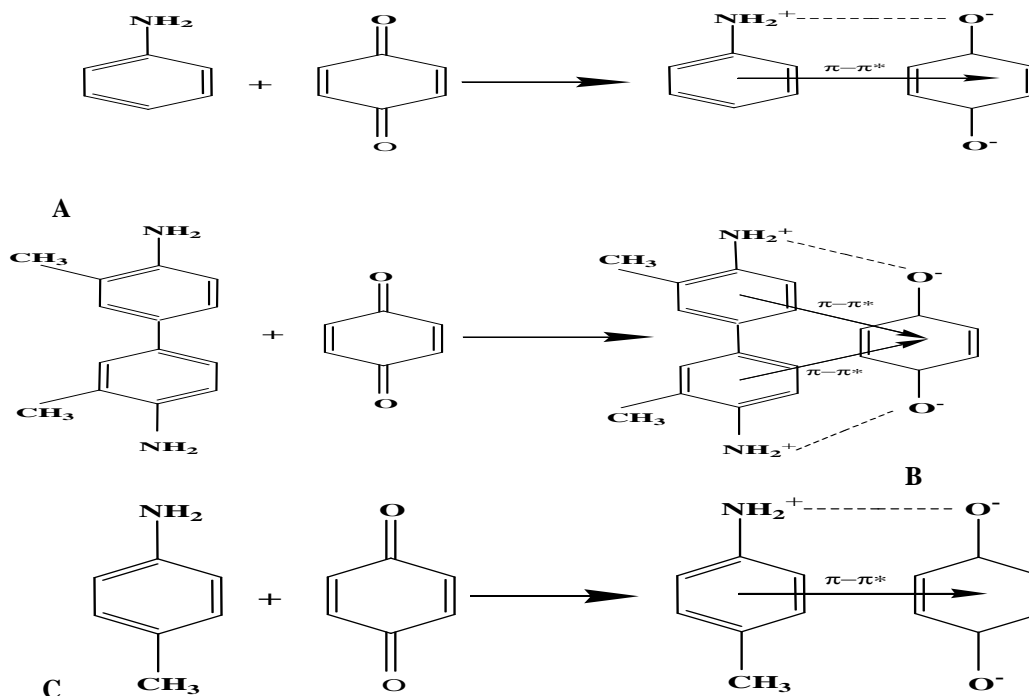
complex	λ_{CT} nm	K_{CT} mol^{-1}	ϵ_{CT} $\text{mol}^{-1}\text{cm}^{-1}$	E_{CT} eV	I_p mean value	ΔG Kcalmol^{-1}
An-Bq	315	10503	11600	3.948	8.334	5.436
4-Tol-Bq	287	10864	8.347	4.333	8.250	5.467
2-Tol-Bq	295	16915	15.22	4.216	8.158	5.644
8-Hq-Bq	312	25374	4.152	4.012	8.461	6.08
2-At-Bq	270	41479	34.965	4.606	8	6.483

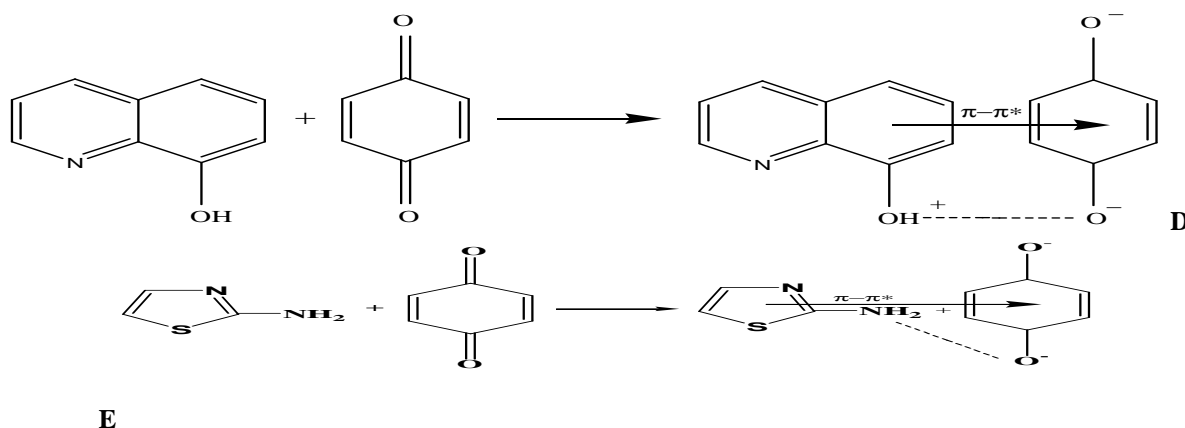
¹H NMR spectra

The proton magnetic resonance, ¹H NMR spectra of the CT complexes of 1,4-benzoquinone with aniline, 4-toluidine, 2-toluidine, 2-aminothiazol and 8-hydroxyl-quinoline were measured in DMSO solvent using tetramethylsilane (TMS) as internal standard. The chemical shifts (δ) of the different types of protons of the acceptor, donors and CT complexes are listed in Table 4. There are changes in the chemical shift values of CT complexes rather than the free donors and acceptor in ¹H NMR spectrum (7). The singlet centered at δ 5.3 ppm of (Bq-An) is attributed to NH₂ group which is observed at δ 3.55 ppm of An (40). ¹H- NMR spectrum of the complexes formed from the interactions between an electron donors with π -acceptor, Hydrogen atom of the NH₂ group of the donors makes intermolecular hydrogen bonding with Oxygen atom of π -acceptor (Scheme 1). The signal of 2H, NH₂ of 2-Tol, 4-Tol and 2-At in of (2-Tol-Bq), (4-Tol-Bq) and (2-At-Bq) CT complexes were observed at δ 4.67, 5.95 and 5.92 ppm resulted from the intermolecular hydrogen bond. The phenolic proton in the 8-hydroxyquinoline usually appears at δ 8.34 ppm. For this complex, it seems to have been shifted, this is resulted the OH of 8-hydroxyquinoline form hydrogen bond with O of acceptor. All the observed proton peaks in the spectra of the starting reactants are also exist in the formed CT complexes spectra with small shifted in values.

Table 4: ^1H NMR spectra for acceptor, donors and their CT complex

Compound	Chemical shift	Assignment
Bq	δ 6.8 ppm	(S, 4H, Ar-H)
An	δ 3.6 ppm	(S, 2H, -NH ₂)
	δ 6.6 ppm	(d, 2H, Ar-H)
	δ 6.7 ppm	(d, 1H, Ar-H)
	δ 7.12 ppm	(d, 2H, Ar-H)
2-Tol	δ 2.14 ppm	(S, 6H, 2x CH ₃)
	δ 4.77 ppm	(S, 4H, 2xNH ₂)
	δ 6.67 ppm	(d, 2H, Ar-H)
	δ 7.11-7.16 ppm	(m, 4H, Ar-H)
4-Tol	δ 2.14 ppm	(S, 3H, CH ₃)
	δ 4.86 ppm	(S, 2H, NH ₂)
	δ 6.50 ppm	(d, 2H, Ar-H)
	δ 6.80 ppm	(d, 2H, Ar-H)
2-At	δ 4.6 ppm	(S, 2H, -NH ₂)
	δ 6.2 ppm	(d, 2H, Ar-H)
	δ 6.7 ppm	(d, 2H, Ar-H)
8-Hq	δ 7.32 ppm	(s, 1H, Ar H)
	δ 7.34 ppm	(s, 1H, OH)
	δ 7.45 ppm	(s, 1H, Ar H)
	δ 8.05 ppm	(d, 1H, Ar H)
	δ 8.08 ppm	(d, 1H, Ar H)
	δ 8.73 ppm	(d, 1H, Ar H)
Bq- An	δ 5.9 ppm	(S, 3H, NH ₂)
	δ 7.3-8.10 ppm	(d, 4H, Ar-H)
Bq- 4 - Tol	δ 2.33 ppm	(S, 3H, CH ₃)
	δ 5.95 ppm	(S, 3H, NH ₂)
	δ 6.72-7.20 ppm	(d, 4H, Ar-H)
Bq- 8 - Hq	δ 7.34 ppm	(S, 1, OH)
	δ 7.32-7.45 ppm	(S, 1H, Ar-H)
	δ 8.05-8.73 ppm	(d, 1H, Ar-H)
Bq 2-At	δ 5.9 ppm	(S, 3H, NH ₂)
	δ 7.2 ppm	(d, 4H, Ar-H)
	δ 8.02-8.51 ppm	(d, 2H, Ar-H)





Scheme 1: Mode of the interaction between 1,4-benzoquinone and donors (A-aniline, B-2-toluidine, C-4-toluidine, D-8-hydroxyquinoline and E-2-aminothiazole)

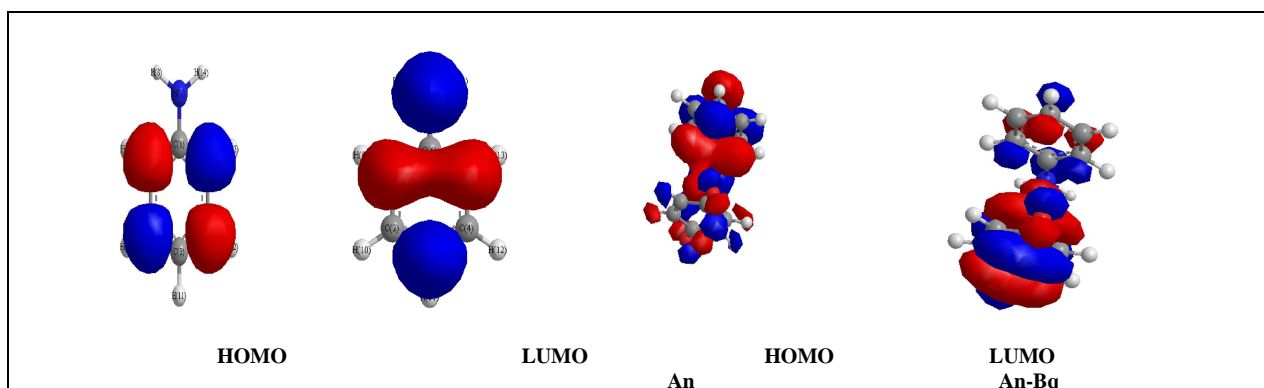
HOMO and LUMO analysis

Molecular orbital and their properties like energy are very useful to the physicists and chemists and their frontier electron density used for predicting the most reactive position in π -electron system and also explained several types of reaction in conjugated system (41). The electronic absorption corresponds to the transition from the ground to the first excited state is mainly described by an electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO)(42). Moreover, the Eigen values of highest occupied molecular orbitals – HOMOs (π -donor) and lowest unoccupied molecular orbitals – LUMOs (π -acceptor) and their energy gap reflect the chemical activity(43). Recently, the energy gap between HOMO and LUMO has been used to prove the bioactivity from intramolecular charge transfer (ICT) (44,45).

Computational analysis of energy levels of HOMO and LUMO orbitals was calculated and the frontier orbitals (HOMO, LUMO) of free donors and CT-complexes are plotted in Fig. 4. The HOMO, LUMO and the results of the energy gap values are reported in Table 5. The most important orbitals in a molecules are the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These orbitals determine the way the molecule interacts with other species. We have calculated the energy gap of the charge complexes figure and the complexes between them figure (4), which support the idea that the aniline, 2-toluidine, 4-toluidine, 2-aminothiazol and 8-hydroxylquinoline act as donors due to high electron density while p-benzoquinone act as acceptors. The reduced HOMO-LUMO energy gap of p-benzoquinone with this donors as well as the charge transfer of chloranilic acid with hexane-1,6-diol (46). The order of stability can be summarized as; An-Bq > 2-Tol-Bq > 2-At-Bq > 8-Hq-Bq > 4-Tol-Bq.

Table 5. HOMO, LUMO and energy gap values of CT-complexes in eV

Compound	LUMO	HOMO	Energy gap
An-Bq	-9.427	-10.623	-1.196
4-Tol-Bq	-3.595	-11.690	-8.365
2-Tol-Bq	-8.474	-9.782	-1.308
8-Hq-Bq	-5.458	-8.126	-2.668
2-At-Bq	0.373	-2.21	-2.583



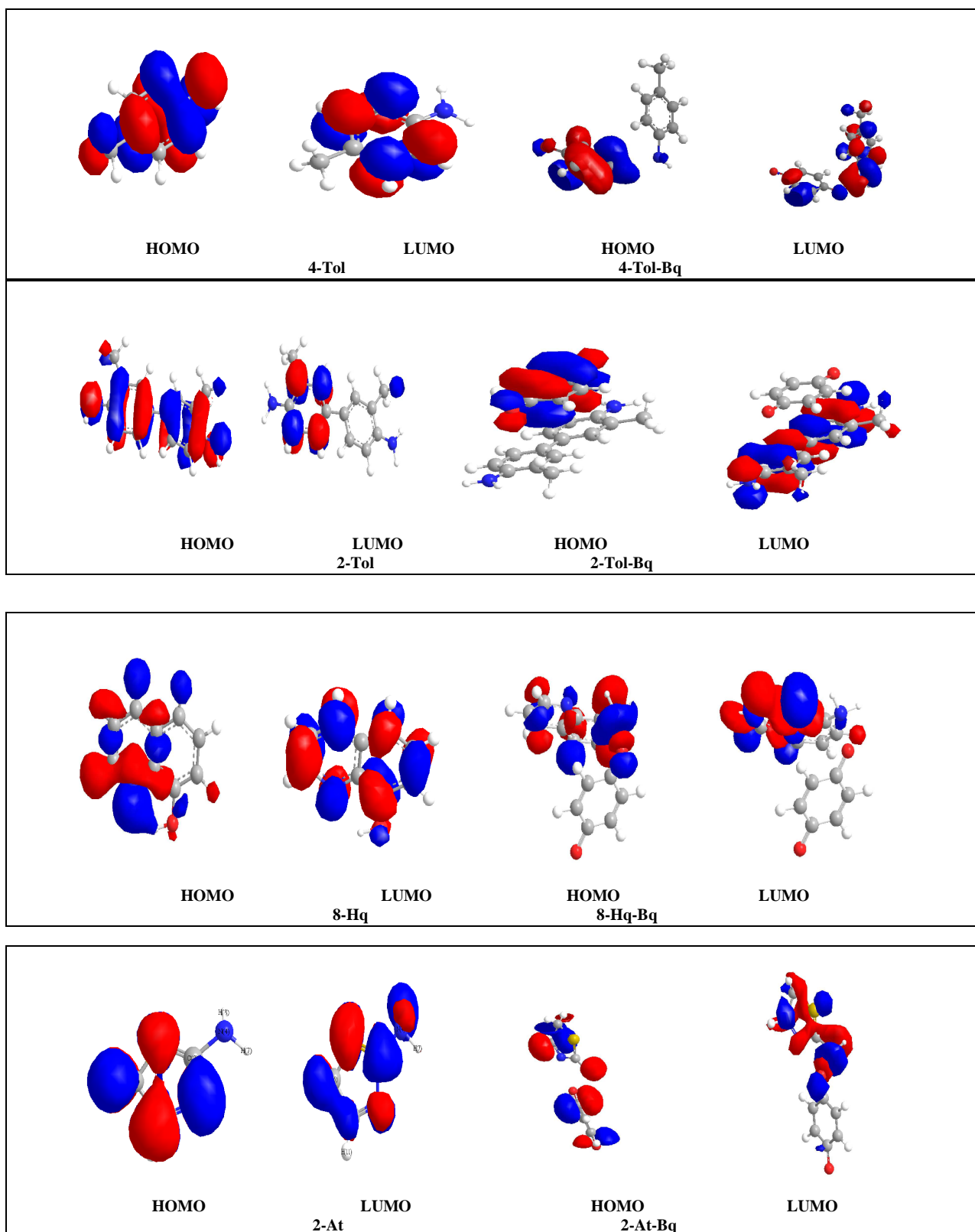


Figure 4. HOMO, LUMO and energy gap values of donors and CT-complex in eV. (Red color represents gain in electron density and blue color represents loss of electron density)

CONCLUSION

The interaction between 1,4-benzoquinone with aniline, 2-tolidine, 4-toluidine, 2-aminothiazol and 8-hydroxylquinoline has been discussed in the solid and solution form. ¹HNMR, Infrared and electronic absorption

spectra investigation indicate that a charge transfer interaction between the donor and acceptor are due to $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ transitions. The formation constant, extinction coefficient, free energy, ionization potential and transition energy of the associated charge transfer complexes were calculated. The HOMO, LUMO and the results of the energy gap values are reported.

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