Physical–Spectroscopic Study of Charge-Transfer Complexes of Some Purine Derivatives with (π) and (σ) Electron Acceptors

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Abstract

Charge-transfer (CT) complexes of adenine (Ade.), guanine (Gua.), xanthine (Xan.), and inosine (Ino.) as electron donors with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 2,3,5,6-tetrabromo-1,4-benzoquinone (Bromanil)(BA) as π – electron acceptors and iodine (Iod.) as σ – electron acceptor were studied and their electronic spectra recorded .In each case one (CT) band was observed and recorded. These spectroscopic investigations made in ethanol solvent at (20°C) temperature. The values of equilibrium constant (K_{CT}), change in standard free energy ($\Delta G°$), molar extinction coefficient (ε_{CT}), absorption band energy ($h\nu_{CT}$) of CT complexes and the association energy of the CT complexes-excited state (W) were calculated and studied with discussed. The ionization potential of the donors (I_P) were calculated and discussed from the CT complex band lowest energy. The oscillator strength (f_{CT}), transition dipole moment (μ_{CT}) and resonance energy (E_R) were also calculated and discussed.

Keyword: Charge–transfer complexes, purine derivatives, DDQ, oscillator strength.

دراسة طيفية فيزيائية لمعقدات انتقال – الشحنة لبعض مشتقات البيورين مع مستقبلات الإلكترون (π) و (σ)

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الخلاصة:

درست معقدات انتقال – الشحنة لواهبات الإلكترون في كل من الأدنين ، الكوانين، الزانثين والانوسين مع 3,2– داي كلورو–6,5 – داي سيانو– 4,1 – بنزوكوينون (DDQ) و 6,5,3,2 – تترا برومو– 4,1– بنزوكوينون (Bromanil) كمستقبلين من نوع (π) واليود كمستقبل من نوع (σ)، كما سجلت أطيافها الالكترونية. وتم تعيين وتسجيل حزمة انتقال – الشحنة لكل معقد. تمت الفحوصات الطيفية في مذيب الكحول الاثيلي وبدرجة حرارة (20) درجه مئوية. حسبت ونوقشت قيم ثابت التوازن (K_{CT})، التغير في الطاقة الحرة القياسية ($\Delta G°$)، معامل الامتصاص المولاري (ε_{CT}) وطاقة تفكك حالة إثارة معقد انتقال – الشحنة (W). كما حسب ونوقش جهد تأين الواهبات(I_P) من حزمة معقد انتقال– الشحنة الأقل طاقة. وأيضاً حسبت ونوقشت قيم شدة التذبذب (f_{CT}) وعزم ثنائي القطب الانتقالي وطاقة الرنين لمعقدات انتقال–الشحنة المتكونة.

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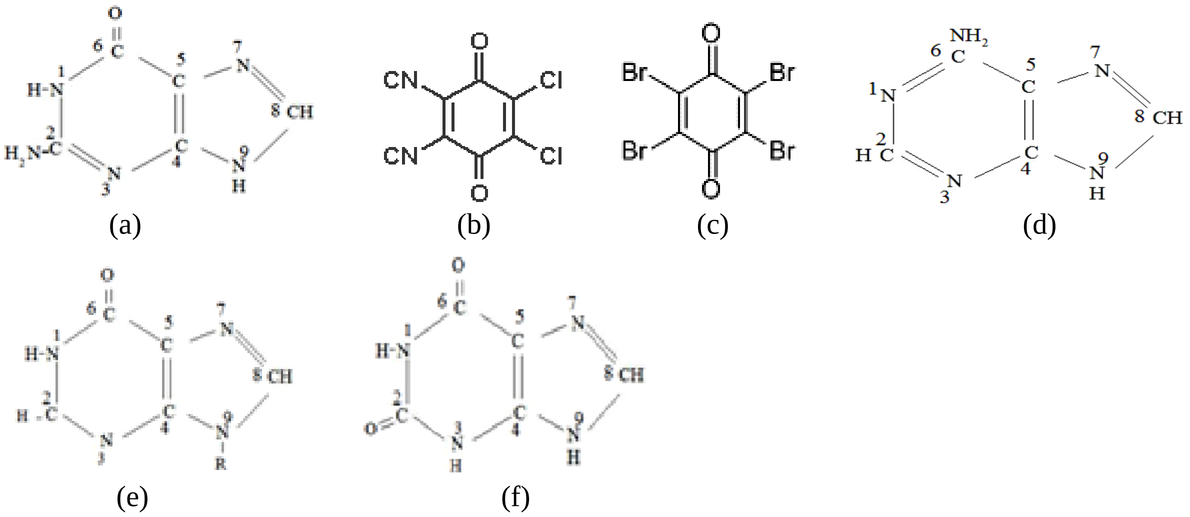
Introduction

The pervious spectral studies on different kinds of nitrogenic bases and aminoacids have included of the electronic, infrared, nuclear magnetic resonance, mass spectrometry, and other spectroscopic methods[1–5]; complexation with various metal ions in ethanolic solutions, and charge–transfer (CT) complexes with various electron acceptors in chloroform and other solutions [6 – 8].

In this work, spectrophotometric studies have been carried out for charge-transfer complexes of 2,3– dichloro–5,6–dicyno–1,4–benzoquinone (DDQ), 2,3,4,5,6–tetrabromo–1,4–benzoquinone (Bromanil) (BA) and iodine (Iod.) with adenine (Ade.), guanine (Gua.), xanthine (Xan.) and inosine (Ino.) in ethanol solvent at (20^oC). The equilibrium constant of charge–transfer complex (K_{CT}), molar extinction coefficient of charge–transfer complex (ε_{CT}), absorption band energy of charge–transfer complex ($h\nu_{CT}$), dissociation energy of charge–transfer complex-excited state (W) and ionization potential of the donors (I_p) were calculated.

Experimental

AnalaR ethanol solvent "BDH", acceptors and donors were used 2,3-dichloro-5,6-dicyano-1,4 benzoquinone (DDQ) of "Fluka" 98% purity, and 2,3,5,6-tetrabromo-1-4-benzoquinone (Bromanil) (G.R) of "BDH" and iodine (pure) of "BDH", adenine and guanine, (puriss) of "Fluka" xanthine and inosine (G.R) of "BDH". All donors and acceptors were used without further purification shown in scheme I.



(a) (b) (c) (d)

(e) (f)

Scheme I- Representative structures of compounds (a) DDQ , (b) Bromanil, (c) adenine (d) guanine (e) xanthine and (f) inosine .

Varian DMS 100 UV–Visible spectrophotometer was used to record the electronic spectra using (1cm) quartz absorption cell. The CT complexes of bases of adenine, guanine, xanthine and inosine were investigated with acceptor of DDQ in ethanol solvent spectrophotometrically at wavelength maximum (λ_{max}) of the complex. This limited work is done for the future since the CT complexes of bases with the electronic acceptor were investigated for first time in this study. The measurements of the optical density of CT complexes at their (λ_{max}) were done directly from the preparation of the complexes at (20^0C) temperature. The concentration of acceptor being kept constant in all solutions.

Results and Discussion

The acceptors of DDQ and Bromanil form a light yellow solutions and the iodine forms a light violet solution in the ethanol solvent, whereas all the donors form colorless solutions. Wavelengths of absorbed maximum (λ_{max}) and molar extinction coefficients values of donor or acceptor (ε) and (ε_{CT}) for CT complex in ethanol solvent were determined and summarized in Table 1. DDQ is a strong acceptor having electron affinity (Ea) 1.95 eV [9]. On mixing solutions of acceptors with donors, a distinct color change observed in ethanol solvent under study. Appearance of a new band on mixing solution of DDQ with one of the donors indicates the formation of CT complex. Neither the donors nor the acceptors alone were found to absorb in that region. Electronic spectra of CT complexes of DDQ with various donors Figures (1-4) in ethanol solvent at (20^0C) temperature were recorded and their (λ_{max}), (K_{CT}) and (ε_{CT}) for CT complexes are reported in Table 2.

Table 1- λ_{max} and ε values of donors and accepter in ethanol solvent at 20˚C

λ_{max}/ (nm) (ε / $m^2.mol^{-1}$)			**Com.**
254(1010±5)	**-----**	**202(1500 ±30)**	**Ade.**
243(870±10)	**-----**	**195(510 ±10)**	**Gua.**
259(540±20)	**218***	**198(710 ±10)**	**Xan.**
241(610±20)	**-----**	**199(840 ± 30)**	**Ino.**
sh.285(1230±40) **340(550 ± 20)**	**247(1610±50)**	**215(2320±100)**	**DDQ**
sh.283(1410±50) **292(1750±60)** **360(80 ±5)**	**232(820±40)**	**220(1730±30)**	**BA**
279(1090±80) **351(640±30)** **433(810±50)**	**sh.246(1720±70)**	**220(2100±90)**	**Iod.**

λ_{max} Wavelength of maximum absorption (nm).
ε Molar extinction coefficient.
sh. Shoulder.
***** Not clear-cut shoulder.

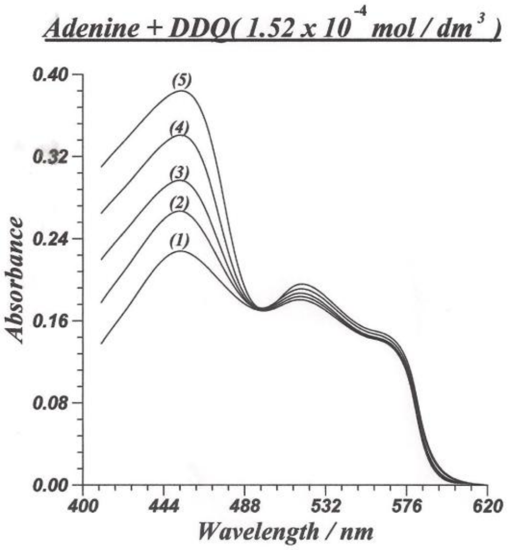


Figure 1- *Electronic spectrum of charge-transfer complex between acceptor DDQ (constant conc.) and adenine donor (variable conc.) at ethanol solvent. Reference cell contain the same concentration of DDQ in the sample cell.*

[Adenine]
(1) 2.93×10^{-3} mol / dm^3
(2) 3.91×10^{-3} mol / dm^3
(3) 4.88×10^{-3} mol / dm^3
(4) 6.84×10^{-3} mol / dm^3
(5) 9.77×10^{-3} mol / dm^3

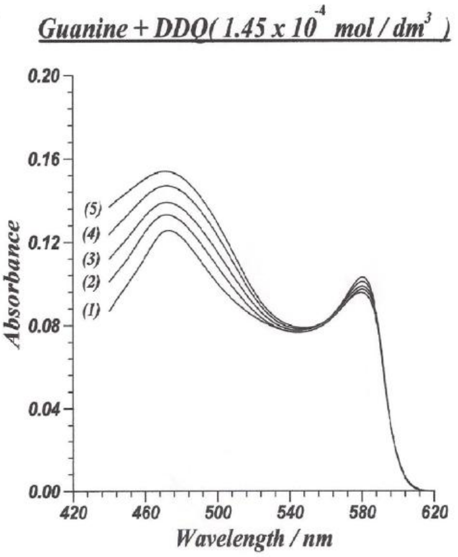


Figure 2- *Electronic spectrum of charge-transfer complex between acceptor DDQ (constant conc.) and guanine donor (variable conc.) at ethanol solvent. Reference cell contain the same concentration of DDQ in the sample cell.*

[Guanine]
(1) 2.09×10^{-3} mol / dm^3
(2) 2.79×10^{-3} mol / dm^3
(3) 3.49×10^{-3} mol / dm^3
(4) 4.89×10^{-3} mol / dm^3
(5) 6.98×10^{-3} mol / dm^3

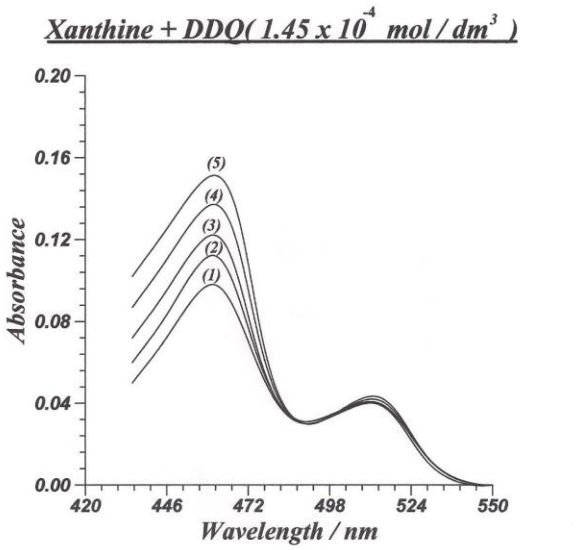


Figure 3- *Electronic spectrum of charge-transfer complex between acceptor DDQ (constant conc.) and xanthine donor (variable conc.) at ethanol solvent. Reference cell contain the same concentration of DDQ in the sample cell.*

[Xanthine]
(1) 2.18×10^{-3} mol / dm^3
(2) 2.91×10^{-3} mol / dm^3
(3) 3.64×10^{-3} mol / dm^3
(4) 5.09×10^{-3} mol / dm^3
(5) 7.26×10^{-3} mol / dm^3

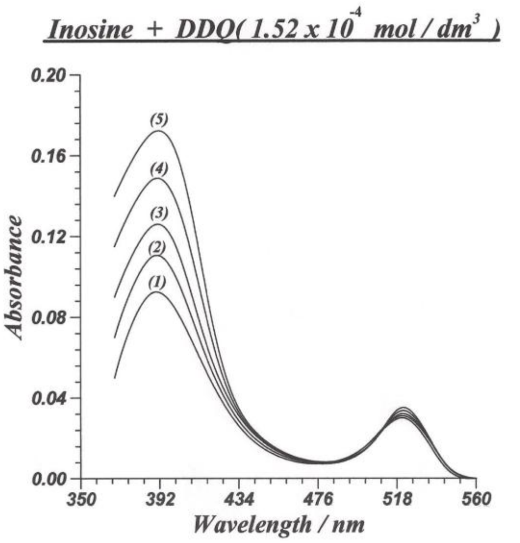


Figure 4- *Electronic spectrum of charge-transfer complex between acceptor DDQ (constant conc.) and inosine donor (variable conc.) at ethanol solvent. Reference cell contain the same concentration of DDQ in the sample cell.*

[Inosine]
(1) 3.00×10^{-3} mol / dm^3
(2) 4.00×10^{-3} mol / dm^3
(3) 5.00×10^{-3} mol / dm^3
(4) 6.99×10^{-3} mol / dm^3
(5) 9.99×10^{-3} mol / dm^3

Table 2- λ_{max}, K_{CT} and ΔG^0 values for CT complexes at 20^0C.

CT C	λ_{max}/nm(Ɛ/m^2.mol^{-1})	K_{CT} / dm^3.mol^{-1}	ΔG^0/ k.J.mol^{-1}
DDQ-Ade.	**453 (380)** [a]	**223.27**	**13.17**
	515	**-------**	**---**
	Sh.561 [b]	**-------**	**---**
DDQ-Gua.	**470 (120)** [a]	**1408.08**	**17.66**
	578 [b]	**--------**	**---**
DDQ-Xan.	**460 (140)** [a]	**463.67**	**14.96**
	512 [b]	**--------**	**---**
DDQ-Ino.	**388 (180)** [a]	**178.93**	**12.64**
	521 [b]	**--------**	**---**
BA-Ade.	**533**	**--------**	**---**
Iod.- Ade.	**452**	**--------**	**---**

a Highest transition energy**.**
b Lowest transition energy**.**

The (K_{CT}) and (ε_{CT}) of CT complexes were determined using modified Benesi-Hildebrand [10] equation given as follows:

$$\frac{[DDQ].\ell}{OD_{CT}} = \frac{1}{K_{CT}\ \varepsilon_{CT}} \cdot \frac{1}{[D_\circ]} + \frac{1}{\varepsilon_{CT}} \ ....(1)$$

Where [DDQ] is the initial concentration of DDQ as electron acceptor, ℓ is the path length of light for absorption cell (L=1cm), OD_{CT} is the optical density of CT complex, [D◦] is the initial concentration of electron donor, K_{CT} is the equilibrium constant of CT complex in solution and ε_{CT} is the molar extinction coefficient of CT complex.

The (K_{CT}) and (ε_{CT}) values are calculated from equation (1) by varying the concentration of donor concentration [D∘] and keeping concentration of acceptor [DDQ] such that [D∘] >> [DDQ]. The plot of ([DDQ]/ OD_{CT}) vs. (1/[D∘]) is given in figures (5 – 8). (ε_{CT}) and (K_{CT}) were calculated from the intercept and slope of these plot.

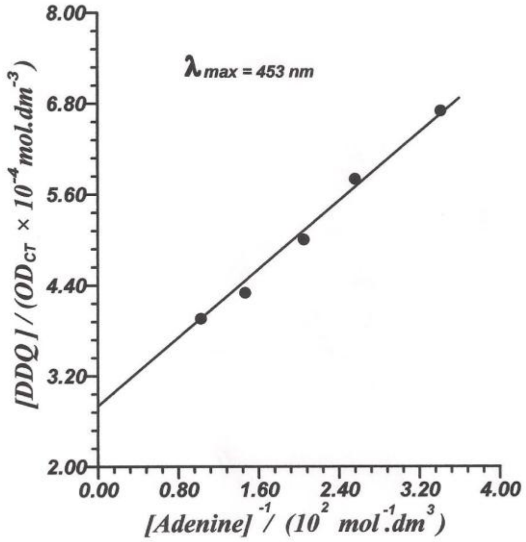


Figure 5- *Application of Bensi-Hildebrand equation for charge-transfer complex between DDQ acceptor and adenine donor.*

Coefficient of Correlation = 0.9965

Linear equation :

$Y = 1.1886 \times 10^{-6} X + 2.6538 \times 10^{-4}$

$\varepsilon_{CT} = 1 / \text{Intercept} = 380 \; m^2.\,mol^{-1}$

$K_{CT} = \text{Intercept} / \text{Slope} = 214.68 \; mol^{-1}.\,dm^3$

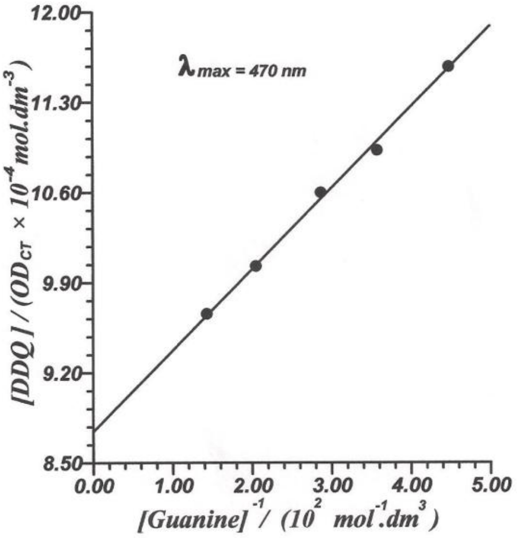


Figure 6- *Application of Bensi-Hildebrand equation for charge-transfer complex between DDQ acceptor and guanine donor.*

Coefficient of Correlation = 0.9984

Linear equation :

$Y = 6.22359 \times 10^{-7} X + 8.76636 \times 10^{-4}$

$\varepsilon_{CT} = 1 / \text{Intercept} = 120 \; m^2.\,mol^{-1}$

$K_{CT} = \text{Intercept} / \text{Slope} = 1408.08 \; mol^{-1}.\,dm^3$

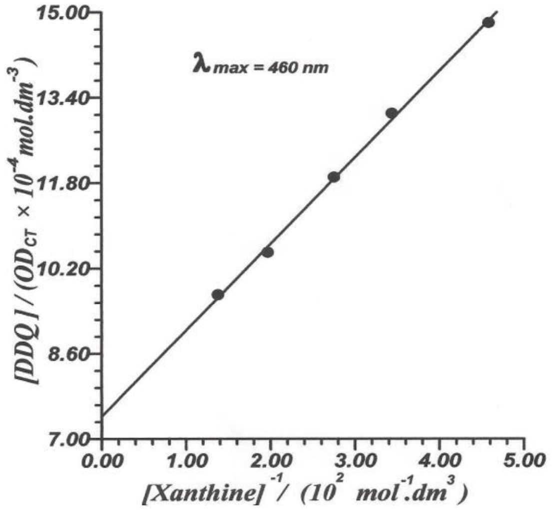


Figure 7- *Application of Bensi-Hildebrand equation for charge-transfer complex between DDQ acceptor and xanthine donor.*

Coefficient of Correlation = 0.9995

Linear equation :

$Y = 1.60599 \times 10^{-6} X + 7.44644 \times 10^{-4}$

$\varepsilon_{CT} = 1 / \text{Intercept} = 140 \; m^2.\,mol^{-1}$

$K_{CT} = \text{Intercept} / \text{Slope} = 463.67 \; mol^{-1}.\,dm^3$

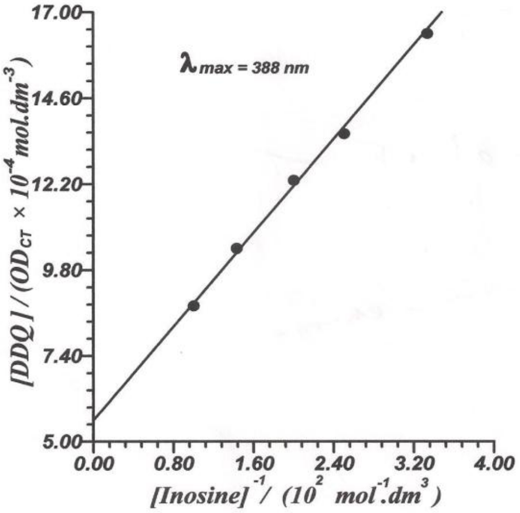


Figure 8- *Application of Bensi-Hildebrand equation for charge-transfer complex between DDQ acceptor and inosine donor.*

Coefficient of Correlation = 0.9989

Linear equation :

$Y = 3.19990 \times 10^{-6} X + 5.72549 \times 10^{-4}$

$\varepsilon_{CT} = 1 / \text{Intercept} = 180 \; m^2.\,mol^{-1}$

$K_{CT} = \text{Intercept} / \text{Slope} = 178.93 \; mol^{-1}.\,dm^3$

According to Mulliken theory [11] wave function of the ground state (1:1) complex is described as follows:

$$\underset{\textbf{Donor}}{\mathbf{D}} \quad + \quad \underset{\textbf{Acceptor}}{\mathbf{A}} \quad \overset{\mathbf{K_{CT}}}{\rightleftarrows} \quad \underset{\textbf{CTC}}{\mathbf{DA}}$$

$$\underset{\textbf{CTC}}{\mathbf{DA}} \quad = \quad \underset{\textbf{CTC at G.S.}}{\mathbf{D,A}} \quad + \quad \underset{\textbf{CTC at E.S.}}{\mathbf{D^{+}\ldots A^{-}}}$$

$$\Psi_G(D,A) = a\Psi_0(D,A) + b\,\Psi_1(D^{+}\ldots A^{-}) \ldots\ldots\ldots\ldots (2)$$

and that of first excited state as follows:

$$\psi_E(D^{+}\ldots A^{-}) = a^{*}\psi_1(D^{+}\ldots A^{-}) - b^{*}\psi_{\circ}(D,A) \ldots (3)$$

Where $\psi_{\circ}$ (D, A) and ψ_1 (D^{+}.. A^{-}) are non bond and dative bond wave functions respectively and (a, b, a^{*} and b*$^{)}$ are constant physical parameters.

For weakly interaction complexes a >> b, the transition energy from ground state to excited state of CT complex could give as follow [12]:

$$h\nu_{CT} = I_P - E_a - W \ldots\ldots\ldots\ (4)$$

Where ($h\nu_{CT}$) is absorption band energy of CT complex, (I_P) is the ionization energy of the donor, (E_a) is the electron affinity of the acceptor and (W) is the dissociation energy of the CT complex in its excited state.

Foster [9] has shown that the frequency of the CT spectra was proportional to the ionization energies of the donors:

$$h\nu_{CT} = aIp + b \ldots\ldots\ldots\ldots\ldots (5)$$

In the present work, a and b from equation (3) are equal to (a = 0.5, b = -1.69 eV) of DDQ acceptor in ethanol solvent [9].

The comparison of the position of absorption bands with the ionization potential of the donor was found by McConnell, Han and platt [13] to facilitated by a equation (6) that was linear for ionization potential between (7-12) eV.

$$h\nu_{CT} = I_P - C_1 + \frac{C_2}{I_P - C_1} \ldots\ldots (6)$$

Where ($h\nu_{CT}$) is transition energy for CT band, (C_1 and C_2) are physical constant parameters of electron acceptor in the solvent (C_1=0.51eV and C_2=1.27eV^2 in ethanol solvent) [9].

According to the equation (4) of the formation CT complexes from two acceptors with one donor, electron affinity (Ea) calculates of acceptor (1) when other values known by the following equation (7):

$$(E_a)_1 = (E_a)_2 + (h\nu_{CT})_2 - (h\nu_{CT})_1 \ldots\ (7)$$

The above equation (7) used to calculate electron affinities of iodine and Bromanil acceptors. The electronic spectrum recorded of CT complex between Bromanil as acceptor with adenine as donor and the absorption band of CT complex was recorded at (533nm) for (Ade.-BA) complex in ethanol solvent. The results of physical constants parameters (a,b,C_1,C_2 and Ea) of Bromanil acceptor were obtained as follow:

a= 0.515 b= -1.708eV C_1=6.410eV C_2 = 1.302eV^2 and Ea = (2.07 ± 0.03)eV

While the absorption band of (Ade.-Iod.) complex recorded at (452nm) in ethanol solvent, the results of physical constants parameters of iodine acceptor obtained as follow:

a =0.602 b = -1.95 eV C_1=5.998eV C_2= 1.685eV^2 and Ea = (2.51 ± 0.03)eV

The calculated electron affinity values of Bromanil and iodine in this work were very agreeable with their values in study of Chen and Wentworth which estimate the values **(2.22± 0.2) eV** for Bromanil acceptor and **(2.56±0.1) eV** for iodine acceptor [14].

The ratios of these complexes are (1:1), and since: (i) the lowest unoccupied molecular orbital LUMO available in DDQ and Bromanil are (π*) molecular orbital and (ii) molecules of donors are very rich in n-electronic pairs, therefore the expected type of electron transition for CT complexes from highest occupied molecular orbital HOMO in donor to LUMO in DDQ or Bromanil acceptors are the transition type of (n→π*), while the LUMO in iodine is the (σ*) molecular orbital, hence the expected type of electronic transition for CT complexes from HOMO in donor to LUMO in iodine is the transition type of (n→σ*) [9,13]. The kinetic of the association of electron donors with electron acceptors have been reported in literature [9].

The variation with K_{CT} values as evident in Table (2) of the formative CT complexes depend on the electronic density factor of nitrogen atom (*) of amino group in adenine and guanine and nitrogen atom of pyrimidine ring which was steric hindrance lower in xanthine and inosine. The K_{CT} of CT complex (DDQ-Gua.) is about eightfold greater than those of (DDQ-Ino.) that the HOMO in guanine return to electronic pair of amino group, while the HOMO in inosine return to electronic pair of ($\ddot{N}_3$) atom in pyrimidine ring which is effected by steric hindrance of (–R) group (deoxyribose) and this makes the formation of CT complex difficultly. The high value of K_{CT} of CT complexes for (DDQ-Gua.) complex and (DDQ-Xan.) complex resume the acidic medium presence of them (through the preparation) which do more stability of the formation CT complexes.

(*)According to program [15] of Molecular Orbital Theory, which shows HOMO in the molecules (charge density distribution in the molecules)?

The K_{CT} values of (DDQ-purine) complexes as follow:

K_{CT} – Gua.>K_{CT}–Xan.>K_{CT}–Ade> K_{CT} – Ino.

The negative values of change in the standard free energies of the formative CT complexes (ΔG˚) as evident in Table (2) indicated that the formation of CT complexes were spontaneously.

The ionization potential (I_P) was calculated by using two methods by equations (5) and (6) as evident in Table (3), which also includes determined ionization potential values by Futto, Lifshitz and Urbanski [9, 13]. All these results arrived to agreeable degree greater than 99% nearly.

The calculated ionization potentials values in this work of the donors was with average (7.962 ± 0.23) eV by using of equation (5) and (7.941 ± 0.126) eV by using equation (6), and explain that resume the like molecular structures of donors by contained all molecules on the pyrimidine and imidazole rings as basic in the molecule.

The ionization potentials of the guanine and adenine are lower than those of the xanthine and inosine, this result return to the presence of amino group in 2–position for guanine and 6–position for adenine of pyrimidine ring, which is as donating group of electrons on the ring. This lead to increase electron density on pyrimidine ring, hence the electron in electronic pair on nitrogen atom is more active site to transition from HOMO [9].

The dissociation energies values of the formative CT complexes in its exited states (W) between DDQ as acceptor and purines donors were calculated as evident in Table 3. These results are very approximative with average (3.794 ± 0.043) eV, and explain that resume the like molecular structures of the formative excited states after absorption of light and this was respected and agreeable by using some acceptor with all the formative CT complexes.

The oscillator strength of the complex (f_{CT}) which is a dimensionless quantity used to express the transition probability of the CT band and the transition dipole moment of the complex (μ_{CT}). The results values in Table 4- were calculated from the following expression [16]:

$$f_{CT} = 4.319 \times 10^{-9} \left(\varepsilon_{max} \cdot \Delta\bar{\upsilon}_{1/2}\right) \text{...(8)}$$

$$\mu_{CT} = 9.581 \times 10^{-2} \left(\varepsilon_{max} \cdot \frac{\Delta\bar{\upsilon}_{1/2}}{\bar{\upsilon}_{max}}\right) \text{.......(9)}$$

Where $\Delta\bar{\upsilon}_{1/2}$ is the band half width of absorbance, $\bar{\upsilon}_{max}$ is the wave number at the maximum absorption of the complex.

Table 3- Lowest transition energies values of CT band of donors with DDQ ($h\nu_{CT}$), and dissociation energy of formed CT complex excited states of donors with DDQ (W) & ionization potential of donors (I_P) in 20˚C.

D	$h\nu_{CT}$/eV	W/eV	a I_P/eV	b I_P/eV	C I_P/eV
Ade.	**2.2118**	**3.736**	**7.804**	**7.834**	**7.80**
Gua.	**2.1467**	**3.776**	**7.672**	**7.727**	**7.65**
Xan.	**2.4234**	**3.854**	**8.227**	**8.118**	**-----**
Ino.	**2.3816**	**3.811**	**8.143**	**8.086**	**-----**

a Ionization potential were calculated by equation (5).
b Ionization potential were calculated by equation (6).
c Measurements results of ionization potentials from references [9, 13].

Table 4 - $\bar{\upsilon}_{max}$, $h\upsilon_{CT}$, $\Delta\bar{\upsilon}_{1/2}$, f_{CT}, μCT and E_R of CT complex formation between DDQ and purines in ethanol solvent at 20^0C.

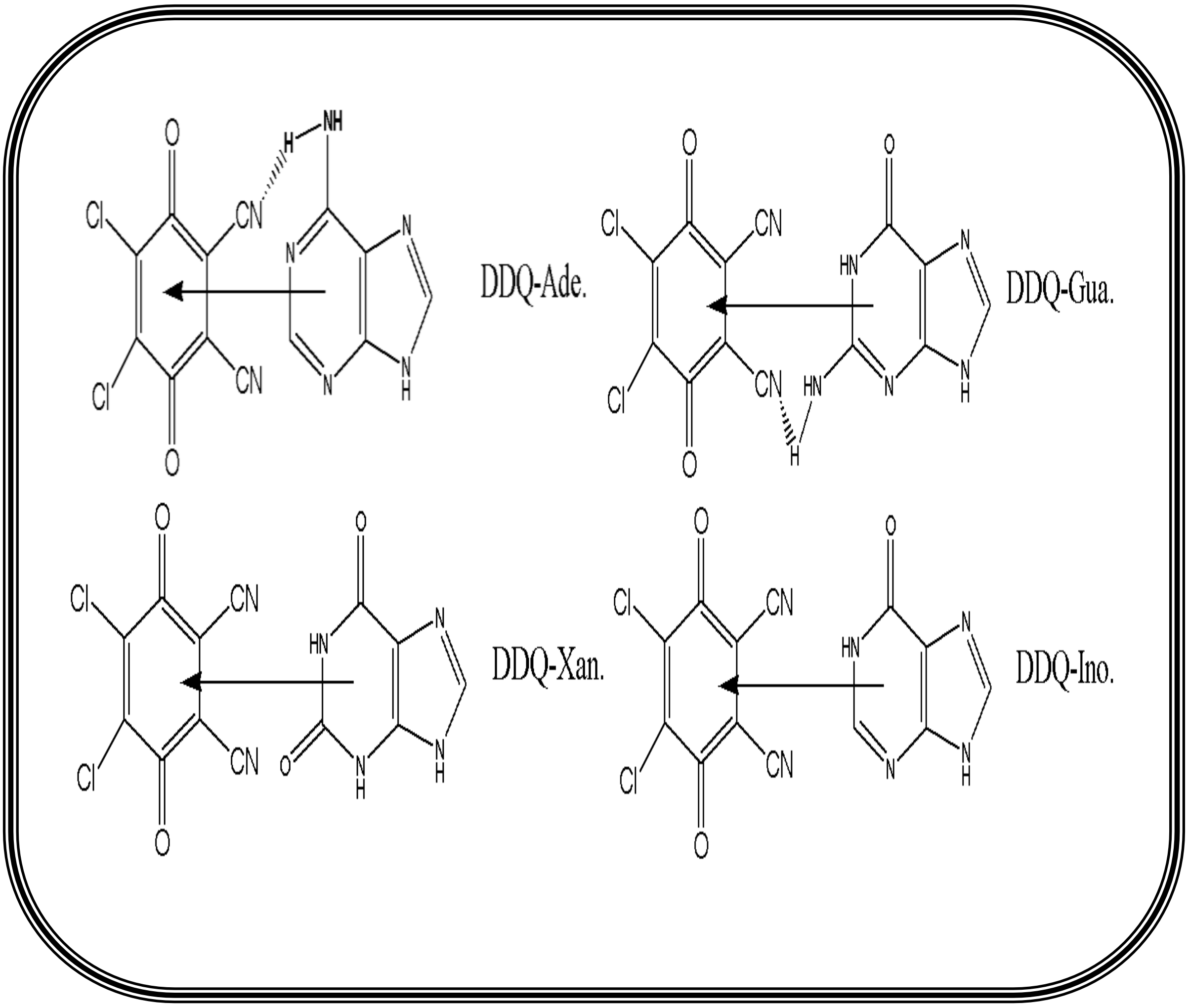
CTC	$\bar{\upsilon}_{max}$/ cm^{-1}	$h\upsilon_{CT}$/ eV	$\Delta\bar{\upsilon}_{1/2}$/ cm^{-1}	$f_{CT}/10^{-3}\,l.mol^{-1}.cm^{-1}$	μ_{CT}/ Debye	E_R/ eV
DDQ-Ade.	22075	2.739	3234	53.07	2.260	0.783
DDQ-Gua.	21378	2.640	5522	28.60	1.691	0.754
DDQ-Xan.	21739	2.697	1609	9.80	0.976	0.771
DDQ-Ino.	25773	3.198	4416	34.30	1.683	0.914

The resonance energy of the complex in the ground state (E_R) has been calculated from relation which is derived theoretically [17]:

$$E_R = \left(\frac{h\nu_{CT} \cdot \varepsilon_{max}}{7.7 \times 10^{-4} + 3.5\, \varepsilon_{max}}\right) \ldots\ldots (10)$$

Where $h\nu_{CT}$ is the transition energy of CT complex.

Returning to Table 4, relative high values of (f_{CT}) for Ade., Ino., and Gua. CT complexes indicate a strong interaction between donor – acceptor pairs, on the other hand the higher values of (μ_{CT}) of DDQ with Ade., Ino. and Gua. suggested the formation of inner sphere complex $D^+ - A^-$. The complex of DDQ with Xan. recorded small (μ_{CT}) suggested the formation of the outer sphere complex D – A [8] as shown in scheme (II). The values of (E_R) for the complexes under study have been given in Table (4) and which, obviously is a contribution factor to the stability constant of the complex (a ground state property) [17].



Scheme II- Charge–transfer structures of Ade., Gua., Xan. and Ino. with DDQ.

Conclusion

In conclusion, it signed two kinds of transitions of charge transfer complexes ($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$) between the donors (Ade., Gua., Xan. and Ino.) and the acceptors DDQ and (BA), on the other hand there is one kind of transition of charge-transfer complexes ($n \rightarrow \sigma^*$) between the donors and the iodine acceptor. The high value of K_{CT} of CT complexes for (DDQ-Gua.) complex and (DDQ-Xan.) complex resume the acidic medium presence of them refer to that its more stable than the other formation CT complexes. The negative values of change in the standard free energies of the formative CT complexes (ΔG°) indicated that the formation of CT complexes were spontaneously. Relative to the high values of (f_{CT}) for Ade., Ino., and Gua. CT complexes indicate a strong interaction between donor–acceptor pairs, and the higher values of (μ_{CT}) of

DDQ with Ade., Ino. and Gua. suggested the formation of inner sphere complex $D^+ - A^-$. The complex of DDQ with Xan. recorded small (μ_{CT}) values suggested the formation of the outer sphere complex D – A.

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