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Application of Charge Transfer Complexation Reaction for the Spectroscopy Determination of Anticonvulsant Drug Primidone

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The interaction of the perimidone drug in solution state with the σ -acceptor iodine, the aliphatic π -acceptor tetracyanoethylene (TCNE) and the aromatic π -acceptor 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) have been studied through the initial formation of ionic intermediate to charge transfer (CT) complex in methanol at room temperature. The spectral studies of the complexes were determined by UV-Vis, and Fourier transform infrared (FT-IR). The stoichiometries of the complexes were determined to be 1:2 and 1:1 ratio by the photometric molar ratio between primidone with π -acceptors and σ -acceptor, respectively. The equilibrium constants (K_{CT}), molar extinction coefficient (ϵ_{CT}) and spectroscopic-physical parameters (standard free energy (ΔG°), and ionization potential (I_p)) of the complexes were determined upon the modified Benesi-Hildebrand equation. The most stable mono-protonated form of perimidone is characterized by the formation of ^+N-H (pyrimidine ring) intramolecular hydrogen bonded. In the high-wavenumber spectral region $\sim 3400\text{ cm}^{-1}$, the bands of the ^+N-H stretching vibrations could be potentially useful to discriminate the investigated forms of perimidone.

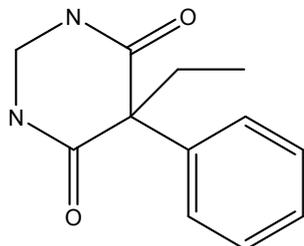
Keywords: Spectroscopic, Charge transfer complexes, Primidone, Iodine, TCNE, DDQ

INTRODUCTION

Charge-transfer (CT) complexes are known to take part in many chemical reactions like addition, substitution and condensation [1-3]. The molecular interactions between electron donors and acceptors are generally associated in the formation of intensity colored charge-transfer complexes which absorb radiation in the visible region [4-10]. Charge-transfer complexation is an important phenomenon in biochemical and bioelectrochemical energy transfer processes [11]. This interest stems mainly from various applications of the CT complexes, including electronic, solar cell, optical devices, and others [12]. On the other hand, the CT-reactions of π -acceptors have been successfully utilized in pharmaceutical analysis [13]. Epilepsy is a chronic neurological disorder characterised by seizures that results from the sudden, disorderly depolarisation of neurons in the brain [14,15]. The

anticonvulsants are a diverse group of pharmaceuticals used in the treatment of epileptic seizures. Anticonvulsants are more accurately called antiepileptic drugs. Primidone (Scheme 1) is a derivative of barbituric acid that resembles phenobarbital in its anticonvulsant activity. After Phenobarbital, the most frequently used anticonvulsant is primidone [16]. Primidone along with phenytoin and phenobarbital is one of the anticonvulsants most heavily associated with bone diseases such as osteoporosis, osteopenia, osteomalacia and fractures [17-19]. It is also used in veterinary to prevent the aggressive behavior and cannibalism of gilt pigs and treatment of nervous disorders in dogs and other animals [20]. We have prepared and spectroscopically investigated the formation of three new CT-complexes produced from the acceptors iodine, DDQ and TCNE in methanol as solvent. This investigation contributes to a deeper understanding the mode of interaction, reaction stoichiometries and structures in the different kinds of CT-complexes. The obtained CT-complexes were structurally characterized using FT-IR and

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Scheme 1. Chemical structure of primidone

electronic absorption spectroscopy. Finally the thermodynamic parameters (ΔG° , E_{CT} , I_p) were also investigated.

EXPERIMENTAL

Reagents and Solutions

All chemicals used were of analytical grade and were used as received. Primidone was obtained from Sobhan pharmaceutical company (Rasht, Iran), while iodine, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) and tetracyanoethylene (TCNE) were purchased from Merck Chemical Co. All chemicals used were of high grade and were used as received.

Spectrophotometric titration measurements were performed for the reactions of primidone with iodine, DDQ and TCNE against methanol as a blank, at wavelengths of 359, 470 and 395 nm, respectively. An aliquot of a standard solution of the appropriate acceptor in MeOH was added to 1.00 ml of 2.0×10^{-4} M primidone, which was also dissolved in MeOH. The total volume of the mixture was 5 ml. The concentration of primidone (Cd) in the reaction mixture was maintained at 2.0×10^{-4} M, whereas the concentration of the acceptors (Ca) changed over a wide range of concentrations (5×10^{-5} - 6×10^{-4} M for all acceptors) to produce solutions with an acceptor molar ratio. The stoichiometry of the molecular CT complexes was obtained from the determination of the conventional spectrophotometric molar ratio according to the known methods [21] using a plot of the absorbance of each CT complex as a function of the Cd:Ca ratio.

Stock solutions of the primidone and each acceptor at a concentration of 1.0×10^{-3} M were freshly prepared prior to each series of measurements by dissolving precisely

weighed quantities in the appropriate volume of the methanol solvent. The stock solutions were protected from light. Solutions for the liquid complexes were prepared by dissolving accurately weighted amounts of primidone and acceptors in an appropriate volume of methanol. The reaction products were obtained by allowing the reactants to react for 24 h. the color of complexes for primidone-iodine, primidone-DDQ, and primidone-TCNE were brown, reddish brown and light yellow, respectively.

Apparatus

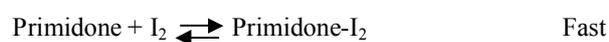
The electronic absorption spectra were recorded in the region of 250-900 nm using UV-Vis spectrophotometer model Biochrom WPA Biowave II with quartz cell of 1.0 cm path length in CH_3OH . The FT-IR spectra of the reactants and the obtained CT-complexes were recorded using KBr discs on Alpha Bruker FT-IR spectrometer. Photometric titrations based on the CT-absorptions at 359, 470 and 395 nm were performed for the reactions of iodine, DDQ and TCNE, respectively, with the donor orimidone in the defined solvent at 25 °C using a Spekol 1300 Analutik Jena UV-Vis spectrophotometer as follows.

RESULTS AND DISCUSSION

Electronic Absorptions Spectra and Determination of Stoichiometry of the Resulting CT Complexes

Interaction of primidone with iodine. The absorption spectra of the reaction between primidone and iodine in methanol are shown in Fig. 1. The spectra obtained for primidone/iodine show the new maximum absorption bands at wavelengths of 359 nm. Instantaneous brown color was obtained on reaction of the colorless primidone solution with the solution of the iodine in methanol. It is observed that the intensity of the band at 460 nm decreased while the intensity of I_3^- ion band at 360 nm increased with elapse of time. The observed time dependent electronic spectrum of the system is due to a transformation of the initially formed outer complex into an inner complex followed by a fast reaction of the resulting inner complex with iodine to form a triiodide ion, as shown below [22-25]:

(i) Formation of the outer complex,



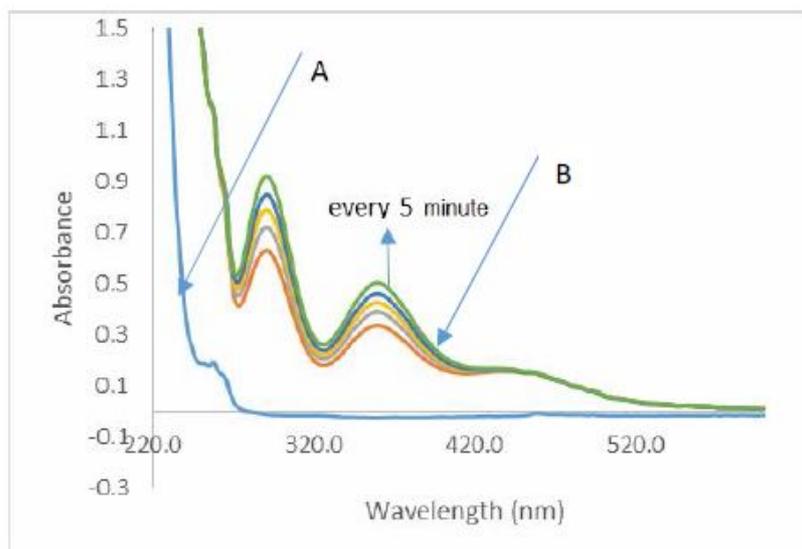


Fig. 1. Electronic absorption spectrum of primidone-iodine reaction in CH₃OH. (A) [primidone] = 1.0 × 10⁻³ M; (B) [Primidone-I₂] = 1.0 × 10⁻³ M.

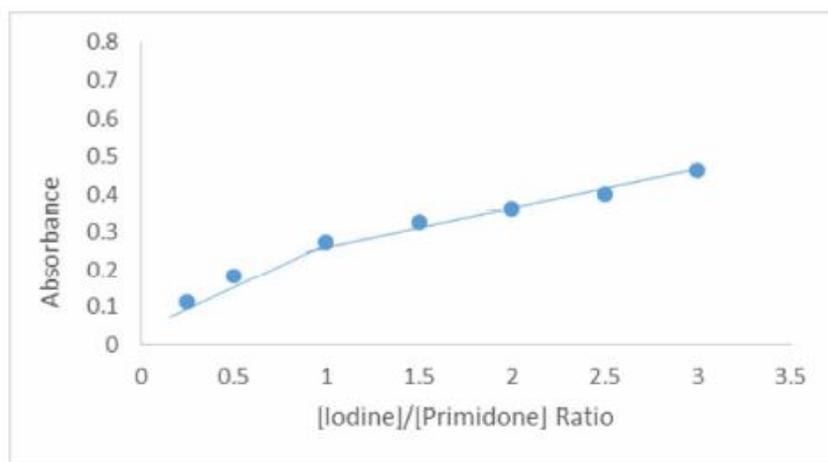
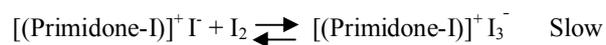


Fig. 2. Photometric titration curve for primidone-I₂ reaction in CH₃OH based on the 359 nm absorption.

This is followed by the formation of inner complex,



which is combined with another iodine molecule to form I₃⁻ as the final product,



Photometric titration measurements based on this CT-complex were performed in order to determine the reaction stoichiometries in CH₃OH (Fig. 2). The results showed that the primidone:iodine molar ratio is 1:1 in the reaction. On

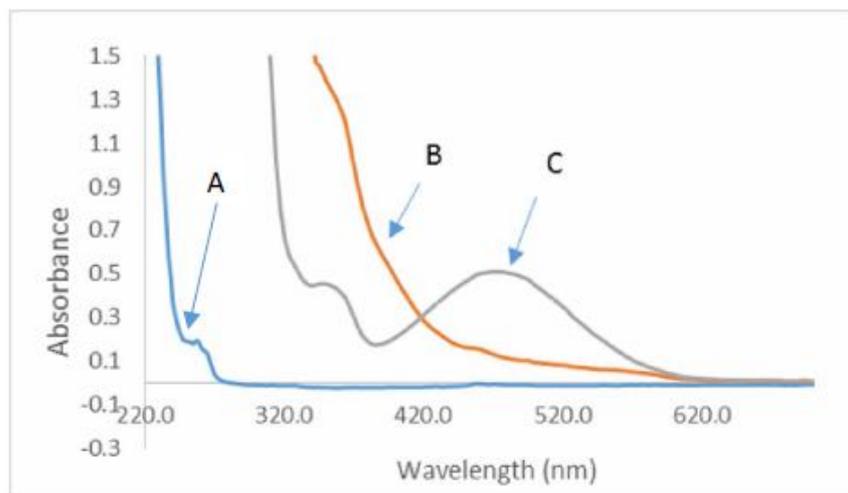


Fig. 3. Electronic absorption spectra of primidone-DDQ reaction in CH_3OH . (A) $[\text{Primidone}] = 1.0 \times 10^{-3} \text{ M}$; (B) $[\text{DDQ}] = 1.0 \times 10^{-3} \text{ M}$; (C) $[(\text{Primidone})(\text{DDQ})_2] = 1.0 \times 10^{-3} \text{ M}$.

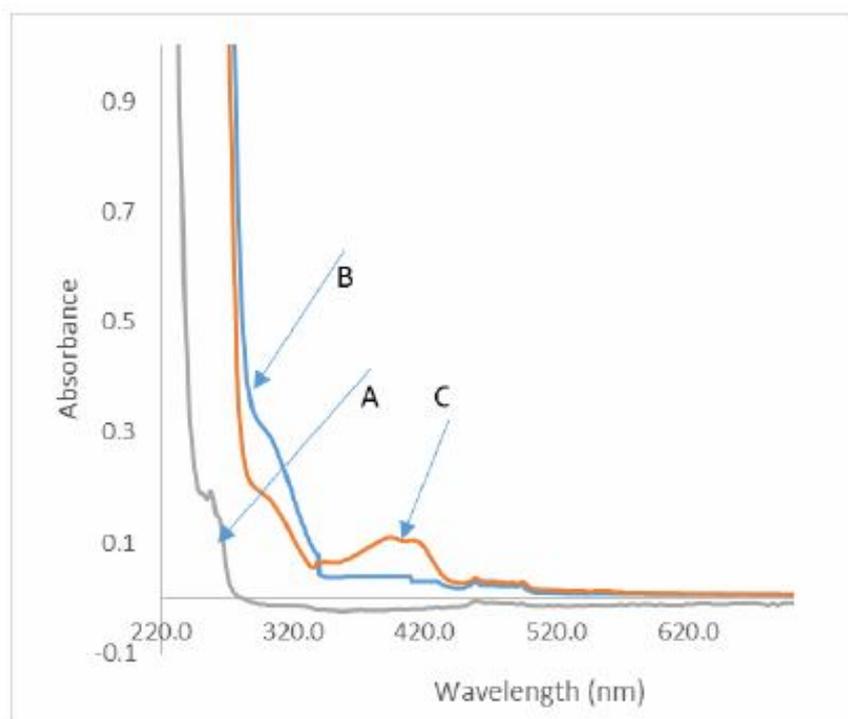


Fig. 4. Electronic absorption spectra of primidone-TCNE reaction in CH_3OH . (A) $[\text{Primidone}] = 1.0 \times 10^{-3} \text{ M}$; (B) $[\text{TCNE}] = 1.0 \times 10^{-3} \text{ M}$; (C) $[(\text{Primidone})(\text{TCNE})_2] = 1.0 \times 10^{-3} \text{ M}$.

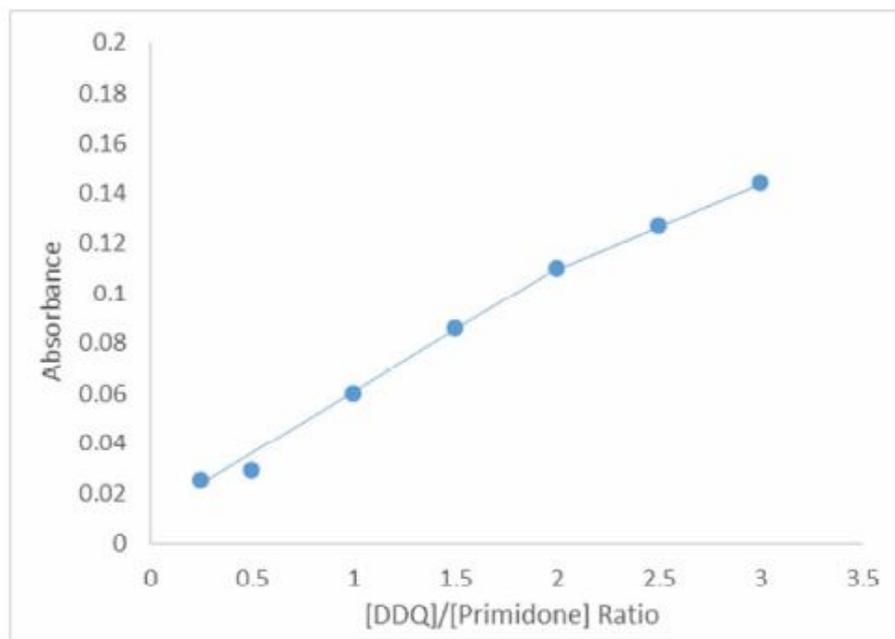


Fig. 5. Photometric titration curve for primidone-DDQ reaction in CH₃OH based on the 470 nm absorption.

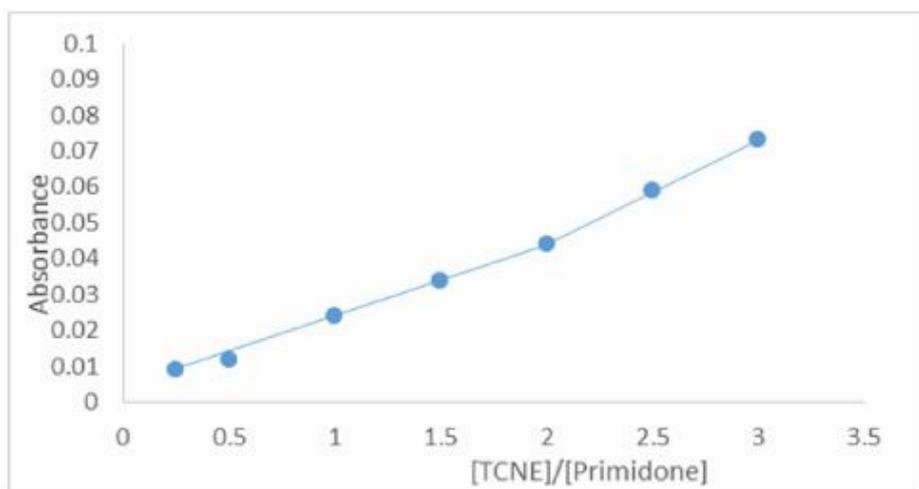
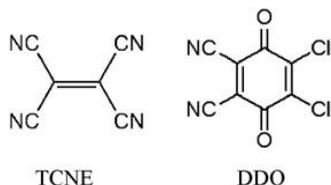


Fig. 6. Photometric titration curve for primidone-TCNE reaction in CH₃OH based on the 395 nm absorption.

the basis of these obtained data, the formed complex can be formulated as [(primidone-I)⁺I₃⁻].

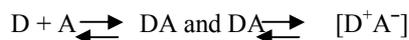
Interaction of primidone with DDQ and TCNE. In

the present study, a mixture of primidone and π -acceptors (DDQ and TCNE) exhibited new absorption bands due to the formation of CT-complexes.



These bands are not present in the spectra of the free reactants and are observed at 470 and 395 nm for the primidone-DDQ and primidone-TCNE systems, respectively. These observations are associated with the change in color, brown for [(primidone)(DDQ)₂] and light yellow for [(primidone)(TCNE)₂], upon mixing of reactants and reflect the electronic transitions in the formed CT-complexes (Figs. 3 and 4).

The CT-complexes formed between donor and π -acceptors may undergo dissociation into ionic intermediate in solvent [26,27]:



Furthermore, photometric titration measurements based on these CT-absorption bands of the CT-complexes (Figs. 5 and 6), confirmed the complex formation in a ratio, primidone:acceptor, of 1:2 for both primidone-DDQ and Primidone-TCNE systems. Stoichiometries of the reactions of the donor under study, primidone, with π -acceptors tetracyanoethylene (TCNE) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) are the same. The formed complexes can be formulated as [(primidone)(DDQ)₂] and [(primidone)(TCNE)₂].

These obtained UV/Vis spectra of the CT-complexes [(primidone)(DDQ)₂] and [(primidone)(TCNE)₂] should be correlated with the electron affinity of each acceptor with donor primidone that is controlled by many factors, such as molecular geometry, steric hindrance and also the electron withdrawing groups attached to the acceptor.

The electronic absorbance bands of the formed CT-complexes [(primidone)I⁺I₃⁻], [(primidone)(DDQ)₂] and [(primidone)(TCNE)₂] in CH₃OH solvent are given in Table 1. Photometric titration measurements demonstrate that the donor-acceptor molar ratio is variable depending on the type of acceptor.

Determination of formation constant (K_{CT}) and molar extinction coefficient (ϵ_{CT}). The values of the

formation constant (K_{CT}) and molar extinction coefficient (ϵ_{CT}) for the formed CT-complexes of donor primidone with iodine, DDQ and TCNE in CH₃OH were calculated at 25 °C.

The 1:1 modified Benesi-Hildebrand Eq. (1) [28] was used for the complex [(primidone)I⁺I₃⁻]:

$$\frac{A_0 D_0 l}{A} = \frac{1}{k\epsilon} + \frac{A_0 + D_0}{\epsilon} \quad (1)$$

The corresponding spectral parameters for the 1:2 complexes [(primidone)(DDQ)₂] and [(primidone)(TCNE)₂] were calculated using the Eq. (2) [29]:

$$\frac{(A_0)^2 D_0 l}{A} = \frac{1}{k\epsilon} + \frac{A_0 (A_0 + 4D_0)}{\epsilon} \quad (2)$$

where A_0 and D_0 are the initial concentrations of the acceptors and donors, while A is the absorbance of the CT-band and l is the light path length (1 cm).

The obtained data from these calculations are given in Table 2. Plotting the values of $A_0 D_0 l/A$ vs. the values of $(A_0 + D_0)$ of Eq. (1) and plotting the values of $(A_0)^2 D_0 l/A$ vs. the values of $A_0 (A_0 + 4D_0)$ of Eq. (2) for the formed complexes exhibit the straight lines that support our conclusion of the formation of the complexes, Figs. (7, 8 and 9). In these plots, the slope and intercept for each case are $1/\epsilon$ and $1/\epsilon K_{CT}$, respectively.

These complexes show high values of both the formation constant (K_{CT}) and the molar extinction coefficient (ϵ_{CT}). These high values reflect the high stability of the complexes as a result of high donation of the primidone containing nitrogen heteroatom and hydroxyl groups. The formation constants are strongly dependent on the nature of the used acceptors including the type of electron withdrawing substituents such as cyano and halo groups.

Determination of standard free energy changes (ΔG°). The free energy changes ΔG° values of complexation were calculated from the formation constant according to the Eq. (3) [30,31]:

$$\Delta G^\circ = -RT \ln K_{CT} \quad (3)$$

Table 1. Spectroscopic Data for the CT-complexes of Primidone with Acceptors I₂, DDQ and TCNE

Complex	Color	Absorption (nm)	Stoichiometry (donor:acceptor)
[(primidone)I] ⁺ I ₃ ⁻	Brown	359	1:1
[(primidone)(DDQ) ₂	Reddish brown	470	1:2
[(primidone)(TCNE) ₂	Light yellow	395	1:2

Table 2. Spectrophotometric Results for Primidone CT-complexes in CH₃OH

Complex	K _{CT} (M ⁻¹)	-ΔG° (cal mol ⁻¹)	E _{CT} (ev)	I _p	ε _{CT} (M ⁻¹ cm ⁻¹)
[(Primidone)I ₂]	2.33 × 10 ⁴	2.5 × 10 ⁴	3.15	7.77	3.048 × 10 ³
[(Primidone)(DDQ) ₂]	6.26 × 10 ⁷	4.4 × 10 ⁴	2.65	7.27	1.698 × 10 ³
[(Primidone)(TCNE) ₂]	1.43 × 10 ⁷	4.0 × 10 ⁴	3.15	7.76	0.856 × 10 ³

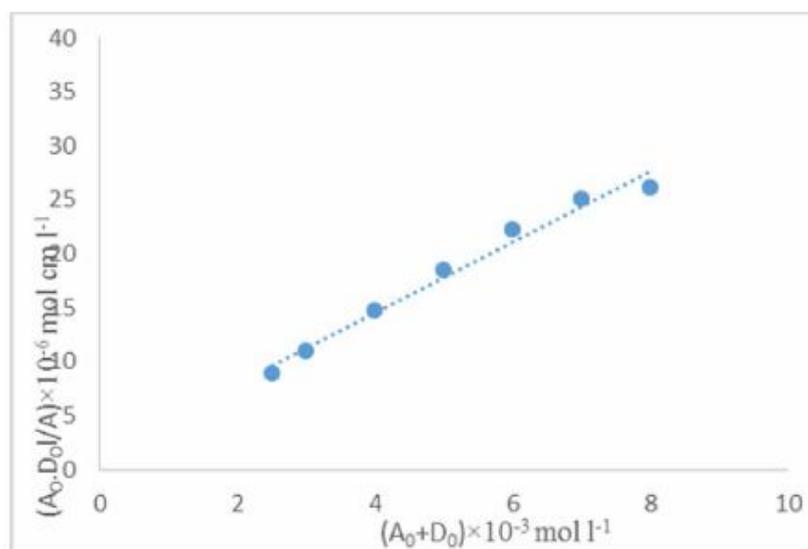


Fig. 7. The modified Benesi-Hildebrand plot of [(Primidone)(Iodine)] charge transfer system in methanol solvent at 360 nm.

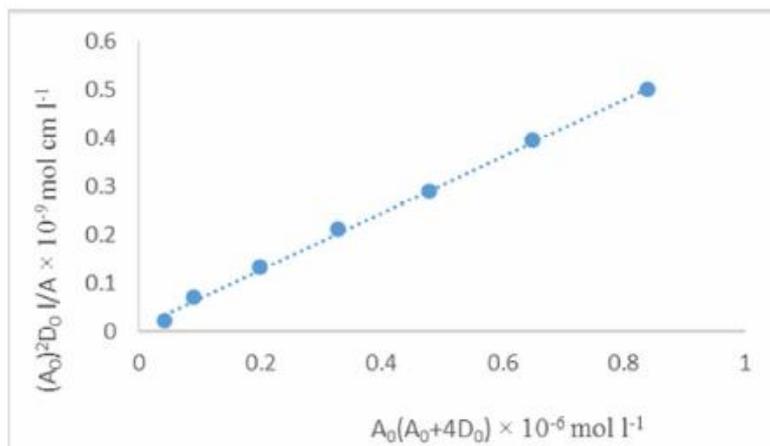


Fig. 8. The modified Benesi-Hildebrand plot of [(Primidone)(DDQ)₂] charge transfer system in methanol solvent at 470 nm.

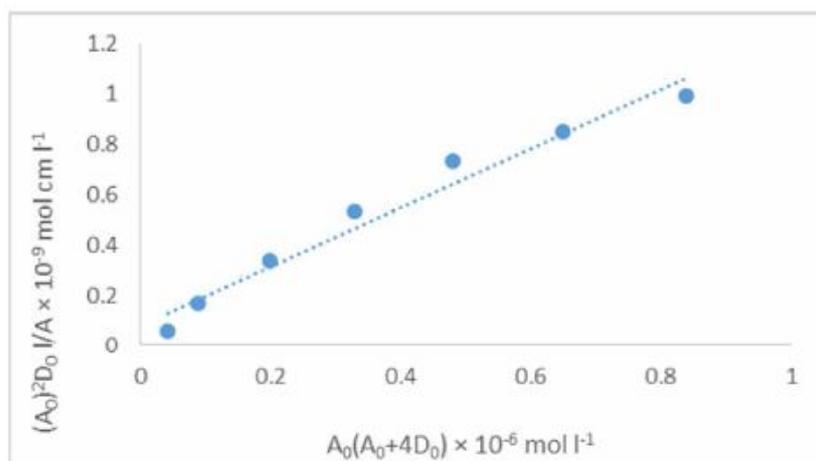


Fig. 9. The modified Benesi-Hildebrand plot of [(Primidone)(TCNE)₂] charge transfer system in methanol solvent at 395 nm.

where ΔG° is the free energy of the formed CT-complexes; R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}$), T is the temperature in Kelvin degrees and K_{CT} is the formation constant of the complexes (l mol^{-1}) at room temperature. The values of ΔG° of the complexes are given in Table 2, which indicate exothermic processes.

Determination of energy (E_{CT}) and ionization potential (IP) of the charge-transfer complex. The

ionization potential of the free donor was calculated from the CT energies of the complexes CT bands using Eq. (4) [32-34]. The values are given in Table 2.

$$E_{CT} = I_p - 5.2 + \frac{1.5}{I_p - 5.2} \quad (4)$$

The energy of the charge-transfer complexes, ECT is

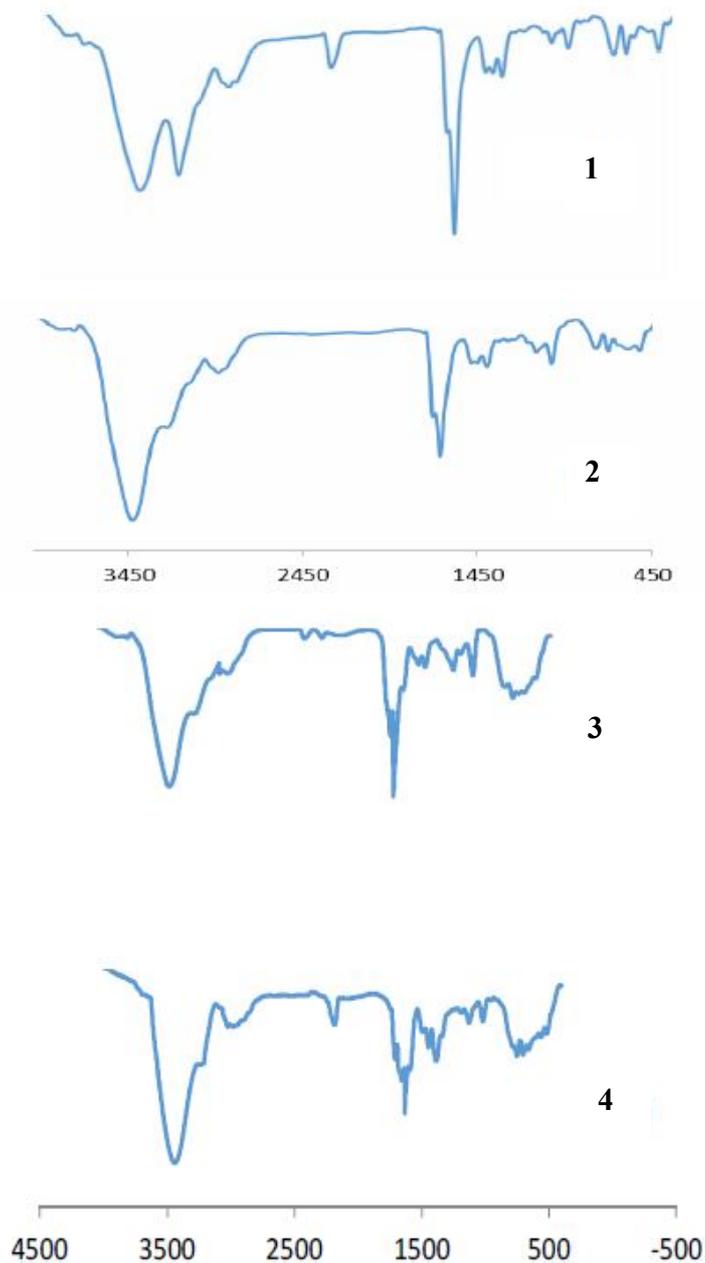


Fig 10. FT-IR spectra for (1) primidone and (2) primidone-iodine, (3) primidone-DDQ, and (4) primidone-TCNE complex systems.

calculated using the following equation, Eq. (5) [35-37]:

$$E_{CT} = (h\nu_{CT}) = \frac{1243.667}{\lambda_{CT} (nm)} \quad (5)$$

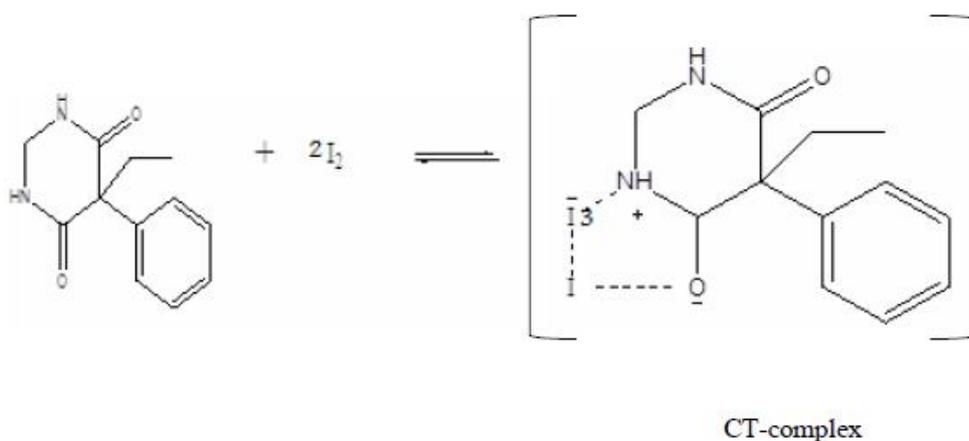
where λ_{CT} is the wavelength in nm corresponding to the complexation band formed between donor and acceptor. The values are given in Table 2.

Infrared absorption spectra. The FT-IR absorption

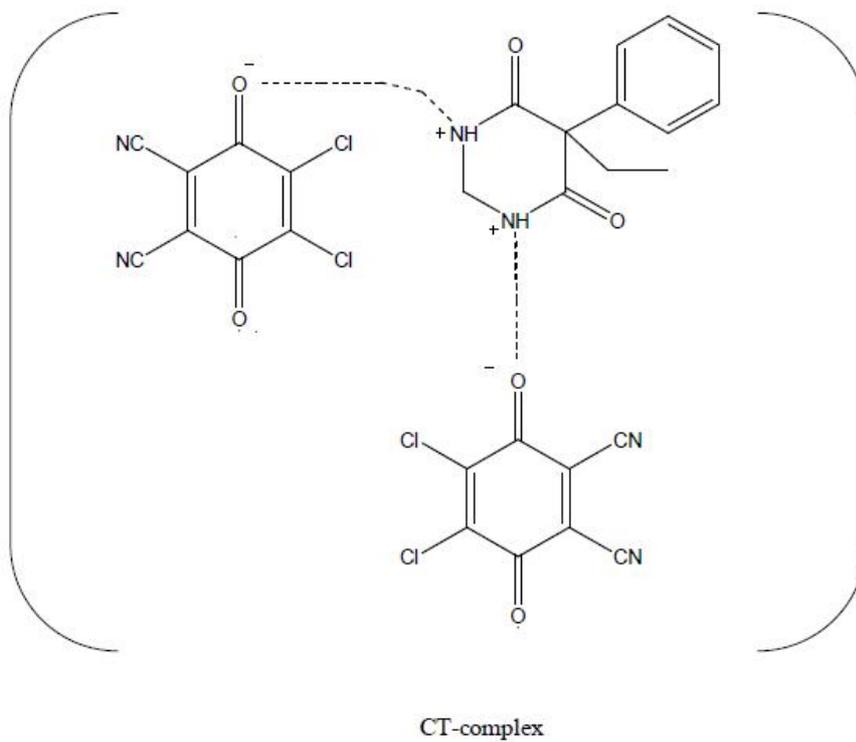
Table 3. FT-IR Wavenumbers (cm^{-1}) and Tentative Band Assignments for Primidone, (Pri) I_2 , (Pri)(DDQ) $_2$, and (Pri)(TCNE) $_2$

Primidone	(Primidone) I_2	(Primidone)(DDQ) $_2$	(Primidone)(TCNE) $_2$	Assignments
3433, br	3428, br	3438, br	3438, br	$\nu(\text{O-H})$; H bonded
3216, s	3220	3222	3228	$\nu(\text{N-H})$
2935	2938			$\nu(\text{C-H})$
2359		2356		H-bonding
		2217, w	2181, w	$\nu(\text{CN})$
1665, s	1664, m	1660, m	1659, m	$\nu(\text{C=O})$
1489	1485			$\delta(\text{CH}_2)$
1449		1449	1445	$\delta(\text{CH}_2)$
1398	1397	1397	1384	$\delta(\text{CH}_3)$
1119	1114		1127	$\nu(\text{C-C}_2\text{H}_5)$
1026	1027	1019	1018	$\beta(\text{CH})$
770	771	751		$\gamma(\text{C=O})$
700	700	702	702	$\rho(\text{CH}_2)$

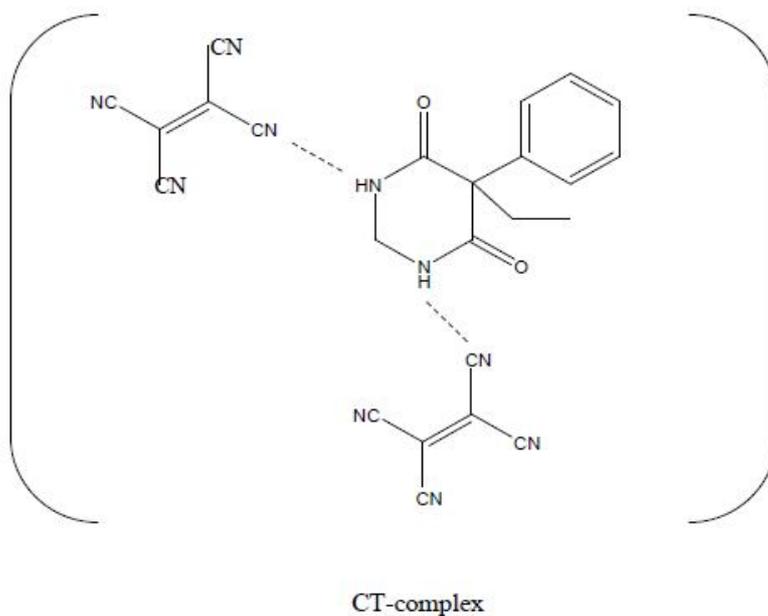
br: broad; s: strong; m: medium; w: weak; ν : stretching; β : in-plane bending; δ : deformation; γ : out of plane bending; ρ : rocking.



Scheme 2. The proposed structure for the [(primidone) I^+] I_3^- complex



Scheme 3. The proposed structure for the [(primidone)(DDQ)₂] complex



Scheme 4. The proposed structure for the [(primidone)(TCNE)₂] complex

spectra of the donor primidone and the formed complexes are shown in Fig. 10. Assignments of the characterized bands in the FT-IR spectra of primidone and CT-complexes are given in Table 3. These assignments are based on the comparison of the spectra of the formed products with the spectra of the reactants, the donor primidone and acceptors DDQ and TCNE. However, the bands of the donor and acceptors in the spectra of complexes show small shifts in wavenumber values and intensities compared with those of the free donor and acceptors. These changes could be understood on the basis of the expected symmetry and electronic structure modifications upon the formation of CT-complexes.

Hydrogen bond formation in all CT-complexes was confirmed with observation of medium to broad bands around 3430 cm^{-1} in the vibrational region of $\nu(\text{O-H})$ and medium to weak bands around 2360 cm^{-1} in the vibrational region of $\nu(\text{N-H})$ [38]. The $\nu(\text{N-H})$ vibration of the free primidone has a strong absorption at 3216 cm^{-1} while the absorption intensities in this vibrational region have been decreased in all formed complexes. These changes in $\nu(\text{N-H})$ upon complexation clearly support involvement of the nitrogen atoms of the donor primidone in the CT-interaction processes. In the interaction with iodine molecule, the observed shift in both C=O and NH peaks indicated the participation of these bands. These observations suggest that electron transfer might have been occurred to form the corresponding triiodide complex. The significant shift of the CN stretching frequency from 2224 cm^{-1} towards lower frequency (2181 cm^{-1}) in [(primidone)(TCNE)₂] is indicative of charge transfer from primidone to π^* of CN group of TCNE which leads to weakening of this bond. For DDQ, the CO stretching frequency appeared at 1685 cm^{-1} in the free acceptor was shifted and emerged with 1660 cm^{-1} in [(primidone)(DDQ)₂] upon complex formation.

Based on the results obtained, the mechanisms suggested for the complexation between primidone donor and acceptors are shown in Schemes 2, 3 and 4.

CONCLUSIONS

Charge-transfer complexes of the donor primidone with each of the electron acceptors iodine, TCNE and DDQ are studied in CH_3OH at $25\text{ }^\circ\text{C}$. We were able to prove the

complex structures. Strong evidences were obtained regarding the CT-interactions based on electronic and vibrational absorption data. These involve comparison between the electronic absorptions and bond vibrations of all reactants before and after complexation. We were able to show that the reaction stoichiometry is not the same for all acceptors. The formed CT-complexes were shown to have the formulas: [(primidone)I₃]⁺, [(primidone)(DDQ)₂] and [(primidone)(TCNE)₂]. Our obtained results indicate that the nitrogen atoms of primidone are involved in complexation with acceptors. On the basis of the results, the donor-acceptor molar ratio was found to be 1:1, 1:2 and 1:2 for primidone:iodine, primidone:DDQ and primidone:TCNE, respectively. Spectrophotometric results (λ_{max} , K_{CT} , ϵ_{max} , E_{CT} , I_p , ΔG°) for the new formed primidone CT-complexes are dependant on the nature of the acceptor used.

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REFERENCES

- [1] E.M. Kosower, *Prog. Phys. Org. Chem.* 3 (1965) 81 [http://refhub.elsevier.com/S0022-2860\(14\)00988-0/h0005](http://refhub.elsevier.com/S0022-2860(14)00988-0/h0005).
- [2] F.P. Fla, J. Palou, R. Valero, C.D. Hall, P. Speers, *JCS Perkin Trans. 2* (1991) 1925 [http://refhub.elsevier.com/S0022-2860\(14\)00988-0/h0010](http://refhub.elsevier.com/S0022-2860(14)00988-0/h0010).
- [3] T. Roy, K. Dutta, M.K. Nayek, A.K. Mukherjee, M. Banerjee, B.K. Seal, *JCS Perkin Trans. 2* (2000) 531.
- [4] A. Mostafa, H.S. Bazzi, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 74 (2009) 180.
- [5] A. Mostafa, H.S. Bazzi, *J. Mol. Struct.* 983 (2010) 126.
- [6] A. Mostafa, H.S. Bazzi, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 79 (2011) 1613.
- [7] H.S. Bazzi, A. Mostafa, S.Y. AlQaradawi, E.M. Nour, *J. Mol. Struct.* 842 (2007) 1.

- [8] H.S. Bazzi, S.Y. AlQaradawi, A. Mostafa, E.M. Nour, *J. Mol. Struct.* 879 (2008) 60.
- [9] S.Y. AlQaradawi, A. Mostafa, H.S. Bazzi, *J. Mol. Struct.* 1037 (2013) 209.
- [10] A. Mostafa, Nada El-Ghossein, S.Y. AlQaradawi, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 118 (2014) 1012.
- [11] D.K. Roy, A. Saha, A.K. Mukherjee, *Spectrochim. Acta A* 61 (2005) 2017.
- [12] S. Licht, *Sol. Energy Mater. Sol. Cells* 35 (1995) 305.
- [13] H. Tsubomura, R.P. Lang, *J. Am. Chem. Soc.* 83 (1961) 2085.
- [14] M.R. Trimble, *New Anticonvulsants Advances in the Treatment of Epilepsy*, Wiley, New York, 1994.
- [15] A.G. Marson, Z.A. Kadir, D.W. Chadwick, *Br. Med. J.* 313 (1996) 1167.
- [16] M.L. Brown, G.B. Brown, W.J. Brouillette, *J. Med. Chem.* 40 (1997) 602.
- [17] A.M. Pack, M.J. Morrell, *CNS Drugs* 15 (2001) 633.
- [18] H.A. Valsamis, S.K. Arora, B. Labban, S.I. McFarlane, *J. Nutr. Metab.* 3 (2006) 36.
- [19] M.G. Harrington, H.M. Hodgkinson, *J. Roy. Soc. Med.* 80 (1987) 425.
- [20] www.en.wikipedia.org/wiki/primidone.
- [21] D.A. Skoog, *Principle of Instrumental Analysis*, third ed., Saunder College Publishing, New York, 1985 (Chapter 7); E.M. Nour, S.Y. AlQaradawi, A. Mostafa, E. Shams, H.S. Bazzi, *J. Mole. Struct.* 980 (2010) 218.
- [22] U.M. Rabie, M.H. Ab-El-wafa, R.A. Mohamed, *J. Mol. Struct.* 871 (2007) 6.
- [23] M. Pandeewaran, K.P. Elango, *Spectrochim. Acta A* 72 (2009) 789.
- [24] M. Hasani, Alireza, *Spectrochim. Acta A* 65 (2006) 1093.
- [25] E.M. Nour, L.A. Shahada, S.A. Sadeek, S.M. Teleb, *Spectrochim. Acta A* 51 (1995) 471.
- [26] M. Pandeewaran, K.P. Elango, *Spectrochim. Acta A* 69 (2008) 1082.
- [27] R.V. Ball, G.M. Eckert, F. Gutmann, D.K.Y. Wong, *Electroanalysis* 8 (1996) 66.
- [28] H.A. Benesi, J.H. Hildebrand, *J. Am. Chem. Soc.* 71 (1949) 2703.
- [29] A. El-Kourashy, *Spectrochim. Acta A* 37 (1981) 399.
- [30] M. Arslan, H. Duymus, *Spectrochim. Acta A* 67 (2007) 573.
- [31] A.A.A. Boraie, *Spectrochim. Acta A* 58 (2002) 1895.
- [32] G. Briegleb, *Z. Angew. Chem.* 72 (1960) 401.
- [33] G. Briegleb, *Z. Angew. Chem.* 76 (1964) 326.
- [34] S. Moamen, Refat, M. Akram, El-Didamony, Ivo Grabchev, *Spectrochim. Acta A* 67 (2007) 58.
- [35] K.P. Pandeewaran, Elango, *Spectrochim. Acta A* 65 (2006) 1148.
- [36] R. Rathone, S.V. Lindeman, J.K. Kochi, *J. Am. Chem. Soc.* 119 (1997) 9393.
- [37] G. Briegleb, J. Czekalla, *Angew. Chem.* 72 (1960) 401.
- [38] G. Briegleb, *Angew. Chem.* 76 (1964) 326.
- [39] G.A. Geffrey, W. Saenger, *Hydrogen Bonding in Biological Structures*, 2nd ed., Springer-Verlag, Berlin Heidelberg, New York, 1994.