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Multiple and sequential charge transfer interactions occurring in situ: A redox reaction of thiazolidine-2-thione with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

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ABSTRACT

Interaction of thiazolidine-2-thione (T2T) as an electron donor with 2,3-dichloro-5,6-dicyano-1,4benzoquinone (DDQ) as an electron π -acceptor has been studied. Electronic absorption spectra of the system T2T–DDQ in several organic solvents of different polarities have been measured. A charge transfer (CT) complexation has occurred between T2T and DDQ. This CT interaction has led to a redox reaction in which T2T has been oxidized to the corresponding dehydrogenated T2T (T2T-2*H*), meanwhile DDQ has been fully reduced to the corresponding hydroquinone (DDQH₂). However, the two new species, resulting in situ, have been interacted, whereas a CT complex having the formula (T2T-2*H*·DDQH₂) has occurred. IR, ¹H NMR and mass spectra were used for ascertaining the structural formula of the synthesized CT complex. Formation constants (K_{CT}), molar absorption coefficients (ε_{CT}) and thermodynamic properties of this CT interaction in various organic solvents were determined and discussed. The obtained K_{CT} and ε_{CT} values have indicated that T2T-2*H* is a weak CT donor, whereas the formed CT complex has a low stability and it is classified as a contact-type CT complex.

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1. Introduction

Thiazolidine-2-thione (T2T) is one of the heterocyclic organic compounds which are of great importance and different applications due to the -(NH)-(C=S)- grouping and the electron donor properties of N and S atoms. Thus, T2T and its derivatives have diverse pharmaceutical [1–11] and industrial applications [12–16]. T2T has a low molecular weight and it seems having simple structural features, however, it has, interestingly, many structural formulae that can be discussed in terms of isomerism, tautomerism and ionized–unionized forms.

On the other hand, T2T has been widely used [17] as a charge transfer donor of low strength that it is capable to form CT complexes with iodine as a typical σ -acceptor. However, according to our knowledge, till date no previous work has been reported for the interaction of T2T with π -type acceptors. The complexity of this compound (T2T) and the willingness to continue our studies [18–22] concerning the π -type acceptors, have motivated us for this piece of work aiming to study the capability of T2T to form n– π CT complexes.

2. Experimental

2.1. Materials and solutions

The electron donor, thiazolidine-2-thione (T2T), was purchased from Aldrich Chemical Co. The electron acceptor, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Aldrich Co.), was recrystallized from both chlorobenzene and dry methylenechloride. The solvents used viz. 1,4-dioxane, benzene, ethanol (EtOH), methanol (MeOH), acetonitrile (CH₃CN)), *N*,*N*-dimethylformamide (DMF), and dimethyl sulphoxide (DMSO), and the chlorinated solvents (carbon tetrachloride (CCl₄), chloroform (CHCl₃), dichloromethane (CH₂Cl₂), and 1,2-dichloroethane (C₂H₄Cl₂)) were of pure spectral grade (BDH or E. Merck).

2.2. Physical measurements

The electronic absorption spectra were recorded on a Perkin-Elmer Lambda 40 spectrophotometer equipped with a Julabo FP 40 thermostat ($\pm 0.1 \,^{\circ}$ C) using 1.0 cm matched quartz cells. IR spectra of the synthesized solid product were recorded on a Shimadzu IR-408 spectrophotometer. ¹H NMR and mass spectra measurements were carried out in the microanalytical laboratory, Cairo University. Computations were performed making use of both the Benesi–Hildebrand [23] and Scott [24] methods with the aid of two programs based on unweighted linear least-squares fits. Stock

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solutions of the donor or acceptors in proper solvents were freshly prepared prior to use. For determination of the formation constants (K_{CT}) and molar absorption coefficients (ε_{CT}) of the CT complexes by applying the Benesi–Hildebrand [23] and Scott [24] methods, spectra of the CT mixtures were measured after mixing solutions of the donor and acceptor and elapsing the time necessary to reach maximum absorption intensity, whereas the concentration of the acceptor was kept constant, meanwhile, the concentration of the donor varied; at least nine mixtures solutions were prepared for each experiment. The different thermodynamic parameters of the CT complexes were determined by applying Van't Hoff plots [25].

2.3. Synthesis of the solid CT complex

The solid CT complex of the donor (T2T) with the acceptor (DDQ) was synthesized by mixing the required amount of T2T (1.2 g, 0.01 mol) dissolved in 50 ml CH₂CL₂ with appropriate amount of the DDQ (2.27 g, 0.01 mol) in 75 ml CH₂CL₂ in 1:1 mole ratio. The mixture was refluxed for (1/2) h and the resulting complex solution was left standing overnight at room temperature. The separated CT solid complex was filtered and washed several times with minimum amounts of ethanol and then dried (colour, yellow; m.p., decomposed).

3. Results and discussion

3.1. Spectral characteristics of thiazolidine-2-thione (T2T)

Before turning our attention to discuss the interaction of T2T with DDQ, it is worthwhile to recall our very recent study [17] concerning the spectral behaviour of this compound (T2T) intending to use and refer to the established data to assist the discussion and to ascertain the results, herein, for the interaction between T2T and DDQ. It has been reported [17] from the IR and UV-vis spectra and the X-ray studies [17] that the compound T2T exists in the solid state as a hydrogen-bonded thioamide complex (Structure III) (NH···S) formed between the NH of the thione form (Structure I) and the exocyclic sulfur atom. This thioamide complex partially breaks down in solutions giving a mixture of free molecules with dimers or higher combinations. The dimer thioamide complex is formed and originated from the thione form or the thiole one (Structure II), i.e., a tautomerism of thione-thiole forms.



Structures (I) and (II): thione-thiole tautomeres.



Structure (III): dimeric hydrogen-bonded thioamide complex.

The UV–vis absorption spectra of T2T in organic solvents have shown two distinct main spectral bands located at 270–280 nm and 315–343 nm. The first absorption spectral band observed at 270–280 nm has been assigned [17] as an intramolecular charge transfer transition (π – π *) within the thiazoline ring, meanwhile the second band shown at 315–343 nm has been assigned [17] as a n– π * intra-transition originated from the exocyclic sulfur atom



Fig. 1. Electronic absorption spectra of the $C_2H_4Cl_2$ solutions of the compounds: (a) T2T, (b) DDQ and (c) T2T–DDQ mixture at 25 °C. [Compound] = 1.0×10^{-4} mol dm⁻³.

of the thione form of the compound T2T. In addition, it has been demonstrated [17] that the compound T2T exists in solution in two tautomeric forms, the thione (Structure I) and thiole (Structure II), and each form has its unique absorption spectra. However, the two forms do not exist in equilibrium but always one form (mostly the thione form) predominates depending on the solvent polarity. Moreover, it has been reported [17] that according to the MNDO calculation, the difference between the enthalpies of formation of the thione and thiol forms of the unsubstituted potential mercaptothiazole is 56.82 kJ mol⁻¹, which is evidence in favour of the thione form.

3.2. Spectral study of the interaction between T2T and DDQ

Electronic adsorption spectra of $C_2H_4Cl_2$ solution mixture (T2T–DDQ) were recorded in the wavelength range 250–750 nm. A new band which does not belong to the donor (T2T) and the acceptor (DDQ) appeared at 350 nm, cf. Fig. 1.

The compound T2T is an electron donor of n-type [17] owing to its unshared electrons on the nitrogen and the two sulfur atoms, meanwhile DDQ is a well known π -acceptor [18–22,26]. Thus the new band located at 350 nm might be assigned as a charge transfer (CT) absorption band. It has been shown [17] that the spectral behaviours of the individual T2T in different solvents are amazing, whereas, as it will be shown hereafter, the spectral behaviours of the T2T–DDQ interaction are very interesting too.

The electronic absorption spectra of the T2T-DDQ interaction in different organic solvents of different polarities are found to be dependent on both the time and the solvent polarity. The electronic absorption spectra of the T2T-DDQ mixture solution in MeOH (or EtOH), a polar protic solvent, are characterized by developing of a new spectral band at 350 nm which does not instantaneously appeared on mixing the two interacting species. The intensity of this new band is gradually increasing by lapse of time and it reaches its maximum intensity after about 70 min from the time of mixing the two reactants, cf. Fig. 2, but the position of this band (at 350 nm) does not change during this lapse of time. Meanwhile, the electronic absorption spectra of the T2T-DDQ solution mixtures in non-polar chlorinated solvents are characterized by the instant observation of that new spectral band in the range of 340-355 nm, and the intensity of this new band is also gradually increasing by lapse of time without a considerable change in the band positions too. Representative spectra are shown in Fig. 3. This prompted us



Fig. 2. Electronic absorption spectra of the (T2T–DDQ) mixture solution in MeOH at 25 °C. [T2T] = 1.0×10^{-3} mol dm⁻³, and [DDQ] = 4.0×10^{-4} mol dm⁻³.

to undertake a further investigation on this phenomenon of timedependency in correlation with the change of the spectral bands appearing through the interaction of the T2T donor with the π acceptor DDQ. Moreover, this system, T2T–DDQ, was completely tracked and evaluated for the probable occurrence of *ca* chemical reaction.

In general, time-dependency in correlation with the CT interactions is still controversy. Some authors [27–31] have referred that time dependency to the transformation of the CT complex from the outer-sphere, a nonbonding structure, to the inner-sphere dative structure (i.e., $D + A \rightarrow D \cdot A$ outer sphere CT complex $\rightarrow D^+ \cdot A^-$ inner sphere (dative structure)). Other authors [18,32] have referred that time dependency to chemical reactions that take place in some cases between the reacting species, even though it has been suggested [18,32] that these chemical reactions have been occurred via



Fig. 3. Electronic absorption spectra of the (T2T–DDQ) mixture solution in CHCl₃ at $25 \degree C$. [T2T] = $4.0 \times 10^{-4} \mod m^{-3}$, and [DDQ] = $2.0 \times 10^{-4} \mod dm^{-3}$.

initial formation of CT interactions (i.e., $D + A \rightarrow D \cdot A$ outer sphere CT complex $\rightarrow D^+ \cdot A^-$ inner sphere $\rightarrow C$ product of the chemical reaction). Other authors [19–21,33] have showed that the stepwise reduction of the π -acceptors to the corresponding anion radicals ($A^{\bullet-}$) or even to the reduced form (AH) is responsible for the lapse of time. They [19–21,33] have presented suggestions that, in some cases, the reduced forms of the π -acceptors can also act as new acceptors [19,20,34], and in other cases, the oxidized forms of the donors can also act as new donors [19], whereas both the new acceptors and the new donors have resulted in situ during the primary donor–acceptor interactions. Thus, the transformation to these new species (the new donors and acceptors) causes this lapse of time [19–21,33].

Herein, in our case, measurements of the electronic absorption spectra of the T2T–DDQ mixtures solutions in each of studied solvents did not show the characteristic [19,21,35–39] spectral bands of the DDQ anion radicals (DDQ.[–]). In addition, as it will be proved hereafter, investigation of the formed CT solid complex by IR, ¹H NMR and mass spectra has indicated that no chemical reaction that could produce a new species occurred.

Thus, we believe that the observed lapse of time, which is necessary for the CT spectral band of the T2T-DDQ interaction to reach its maximum intensity, might be explained by: (1) dissociation of the dimeric thioamide hydrogen-bonded solid complex (Structure III) in the solutions to its individual molecules, whereas the resulting individual molecules exist in the solutions in two tautomeric forms (thione (Structure I) and thiole (Structure II)). (2) Reduction of the DDQ to its corresponding hydroquinone, i.e., DDQH₂. (3) Simultaneous oxidation of the T2T (either in thione or thiole form) to the corresponding dehydrogenated T2T, i.e., T2T-2H. In turn, the observed CT band is referred to a charge transfer arising from the highest occupied molecular orbital (HOMO) of the resulting dehydrogenated new donor (T2T-2H) to the lowest unoccupied molecular orbital (LUMO) of the resulting reduced new acceptor, DDQH₂, whereas the two new interacting species (T2T-2H and DDQH₂) are resulting in situ through a period of time dependent on the polarity of the solvent used.

Quinones, in general, and DDQ, in specific, are well known [32,40–42] as dehydrogenating agents since the pioneering work [43] published in 1954. Several mechanisms, as shown hereafter, have been suggested [32,42] for these kinds of redox reactions that caused by the action of the quinones as dehydrogenating agents. However, it has been reported [41,42] that in many of these redox reactions involving DDQ, CT complexations have been occurred at least initially.

Dehydrogenation of a substrate (AH_2) by a quinone (Q) is generally represented by Eq. (1):

$$AH_2 + Q \to A + QH_2 \tag{1}$$

Meanwhile, this redox reaction might proceed following one of the following suggested [32,42] mechanisms: (1) by hydride ion transfer to the quinone in the rate-determining step (Eq. (2)) followed by rapid proton transfer from the conjugate acid to the hydroquinone anion (Eq. (3)):

$$AH_2 + Q \xrightarrow{\text{slow}} AH^+ + QH^-$$
 (2)

$$AH^{+} + QH^{-} \xrightarrow{\text{rast}} A + QH_2$$
(3)

(2) By proton catalysis (Eqs. (4)-(6)) in which the protonated quinone (QH⁺) acts as an efficient hydride ion acceptor:

$$Q + H^+ \to QH^+ \tag{4}$$

$$AH_2 + QH^+ \rightarrow AH^+ + QH_2 \tag{5}$$

$$AH^+ \to A + H^+ \tag{6}$$



Fig. 4. Infrared spectra of free T2T donor (a), free DDQ acceptor (b) and T2T–DDQ CT complex (c).

(3) By first formation of stable free radicals that lead to hydride ion transfer (Eqs. (7) and (8)):

$$AH_2 + Q \to AH^{\bullet} + QH^{\bullet} \tag{7}$$

$$AH^{\bullet} + QH^{\bullet} \to AH^{+} + QH^{-}$$
(8)

(4) By ene-reaction between the two species, AH_2 and Q, to give an intermediate adduct (I) (Eq. (9)), followed by a slow base-induced elimination (Eq. (10)):

$$AH_2 + Q \rightleftharpoons^{\text{tast}} I \tag{9}$$

$$I \xrightarrow{\text{Slow}} AH^+ + QH^- \tag{10}$$

(5) By sequential electron-proton-electron transfer which most likely occurs via a CT-complex (Eqs. (11)-(14)).

$$AH_2 + Q \rightleftharpoons AH_2 \cdots Q \tag{11}$$

 $AH_2 \cdots Q \rightleftharpoons AH^{\bullet +} + QH^{\bullet -}$ (12)

 $AH^{\bullet+} + QH^{\bullet-} \xrightarrow{slow} AH^{\bullet}QH^{\bullet}$ (13)

$$AH^{\bullet}QH^{\bullet} \to AH^{+}QH^{-}$$
(14)

However, it is worthy to mention that the aforementioned mechanisms of the dehydrogenation by quinones depend [32,42] on the structure of the substrates and, in particular, on the stability or reactivity of the intermediates.

Herein, in our case of interaction between T2T and DDQ, we are not yet in a position to prove unambiguously one or the other suggested mechanisms which could be applied to this T2T–DDQ redox reaction. However, time dependency of the established dehydrogenation of T2T with DDQ, to yield T2T-2*H* and DQQH₂ via first formation of a CT interaction followed by a redox reaction, has found an adequate explanation.

In turn, we believe that the following reaction pathway (Eqs. (15)-(19)) might be hypothesized for the interaction between the T2T, as a donor, with the DDQ, as an acceptor, meanwhile the multiple and sequential CT complexations involved through this T2T–DDQ interaction has been suggested too:

$$\begin{array}{c} T2T & T2T \\ Thioamide dimer complex \xrightarrow{\rightarrow} Individual free molecules \end{array}$$
(15)

$$T2T(thione) \rightleftharpoons T2T(thiole) \quad (tautomerism) \tag{16}$$

$$T2T + DDQ \rightarrow T2T \cdot DDQ$$
 (first CT interaction) (17)

$$T2T \cdot DDQ \rightarrow T2T - 2H + DDQH_2$$
 (Redox reaction) (18)

$$T2T-2H + DDQH_2 \rightarrow T2T-2H \cdot DDQH_2$$
 (second CT interaction) (19)

Though the chemistry of the DDQ as a dehydrogenating agent is not the only manifested observation but we are the first to show that both the oxidized and reduced form of T2T and DDQ, respectively, resulting in situ through first CT interaction between T2T and DDQ can also interact as a new donor (T2T-2*H*) and a new unconventional π -acceptor (DDQH₂) to yield a new CT complex (T2T-2*H*·DDQH₂) (Eq. (19)). Some evidences to confirm our assumptions will be mentioned hereafter.

3.3. Characterization of the T2T–DDQ solid CT complex:

The IR spectra of the free donor T2T, the free acceptor DDO and the solid complex synthesized from the interaction of T2T with DDQ were measured, cf. Fig. 4. A careful examination of the important observed IR spectral peaks of the solid complex has indicated [14,35-37,44,45] the existence of the dehydrogenated T2T (i.e., T2T-2H; oxidized form) and the reduced form of the DDO (i.e., DDQH₂). Thus, the IR spectra of the complex have showed several peaks located at 1450 and 1070 cm⁻¹ which are characteristic [14,44,45] to the stretching vibrations of v(NH) and v(C=S)of the thione form, respectively, whereas these peaks have previously seen in the free T2T except for some reasonable shift due to the CT complexation. In addition, the IR spectra of this complex do not show peaks in the regions 2800-3000, 2400-2700 and $1640-1690 \text{ cm}^{-1}$ which may characterize [14,44,45] the ν (-CH₂-) of the thiazoline, ν (SH) and ν (C=N) of the thiazol forms, respectively, meanwhile the peak that characterizes [44] to the postulated existence of the v(-C=H-) of the thiazole (the dehydrogenated T2T) may be overlapped with other vibration(s) within the broad peak observed at 3200 cm⁻¹.

Also, the IR spectra of the synthesized complex indicate the existence of the hydroquinone (DDQH₂). Thus, the spectral peaks observed at 2250, 1450 and 890 cm⁻¹ are characteristic [35–37] to the stretching vibrations of C=N, C=C (aromatic) and C-Cl of the hydroquinone, respectively, cf. Fig. 4. In addition, the most remarkable and interesting observation concerning the IR spectra of the (T2T/DDQ) CT complex is the disappearance of the 1670 cm⁻¹ band which characteristics [35-37] to the stretching vibrations of C=O of the free DDO; i.e., the acceptor has no longer been in the quinone form. Instead, a broad peak has been observed at 3200 cm^{-1} which characteristics [35-37] to the OHs (of DDQH₂) that might be associated with a hydrogen-bonding with *ca* the exocyclic S atom of the donor (T2T-2H) in its thione form and/or it might be overlapped with the stretching vibration with first -NH- peaks (of the thione form of T2T-2H) usually appeared at around $3300 \,\mathrm{cm}^{-1}$. However, it is worthwhile to mention that none of the characteristic [35–37] peaks for any of DDQ.⁻, DDQ²⁻, DDQH⁻ (anion radicals or semiguinones) have been observed in the IR spectra of the solid CT complex which provides an evidence for the complete reduction of the DDQ to the corresponding hydroquinone (DDQH₂). In turn, the IR spectral measurements have provided a further evidence for our suggested reaction pathway for the interaction of T2T with DDQ. Accordingly, the structure of the formed $(T2T-2H DDQH_2)$ CT complex might be hypothesized as shown in the following



Fig. 5. Electronic absorption spectra of the $CHCl_3$ solution of the synthesized (T2T–DDQ) solid CT complex at °C.

(Structure IV).



Structure (IV): (T2T-2H·DDQH₂) CT complex.

The electronic absorption spectra of the CHCl₃ solution of the synthesized solid CT complex (cf. Fig. 5) have shown a spectral band at around 350 nm. This band has been previously seen in the absorption spectra of the T2T–DDQ mixture solution in CHCl₃ which have been measured after elapsing the time necessary to reach the maximum band intensity. This provides an additional evidence for the suggested (T2T–DDQ) reaction pathway.

On the other hand, the ¹H NMR and mass spectral measurements of the formed CT complex have provided further evidences for confirming the structure of the formed CT complex (T2T-2H-DDQH₂). In turn, the aforementioned suggested reaction pathway of the interaction between T2T and DDQ has found adequate evidence, too.

The ¹H NMR spectrum (300 MHz) of the CT product in DMSO displays distinct signals characterizing [45] to the suggested (T2T-2H·DDQH₂) CT complex namely: δ (ppm); 3.46 (H, s, NH of thione form), 5.62 (H, broad, 2OH of DDQH₂), 6.97 (H, d, C5 proton of thiazole) and 7.43 (H, d, C4 proton of thiazole). However, broadening of the proton signals of the OHs might be referred to a hydrogen bond [45,46] arising with *ca* exocyclic S atom of the donor (T2T-2H).

Convincing evidence for the structure of the $(T2T-2H \cdot DDQH_2)$ CT complex has been provided by the mass spectra. The mass spectra of the synthesized CT complex have displayed the molecular ion peaks m/z (%) = 345 (0.3), 228 (100) and 117 (0.5) which represent the molecular weights of the species T2T-2H \cdot DDQH_2 (the CT complex), DDQH_2 (the acceptor; hydroquinone) and T2T-2H (the donor), respectively. Moreover, the expected corresponding fragments of the DDQH_2 and T2T-2H species have also been indicated from the other remaining mass spectral ion peaks.

It is worthy to mention that the TLC measurement of the synthesized complex under investigation, T2T-2*H*·DDQH₂, has shown a single peak which indicates the existence of a single compound. Thus, one can suggest that the synthesized CT complex, T2T-2*H*·DDQH₂, has a low stability that is readily decomposed under the influence of the applied high energy of the Mass spectroscopy machine [45] ($ca \ge 70 \text{ eV}$) to its two constituent species; DDQH₂ and T2T-2*H*.

3.4. Association constant (K_{CT}) and molar absorption coefficient (ε_{CT}) of the CT complex resulting from the interaction of T2T with DDQ; (T2T-2H·DDQH₂)

Under the condition [T2T] \gg [DDQ], the electronic absorption spectra of the T2T/DDQ mixture solutions in MeOH were measured. The spectra were measured after elapsing 70 min from the time of mixing the two interacting species, whereas this period of time is necessary to reach the maximum CT band intensity. The absorbance values obtained from the CT band, at $\lambda_{max} = 350$ nm and at different temperatures, 10, 15, 20, and 25 °C, were used for determination of the formation constants (K_{CT}) and molar absorption coefficients (ε_{CT}) of the CT complex (T2T-2H·DDQH₂), making use the well known Benesi–Hildebrand [23] and Scott [24] equations (Eqs. (20) and (21)):

$$\frac{[A]_0}{A} = \frac{1}{K_{\rm CT}\varepsilon_{\rm CT}}\frac{1}{[D]_0} + \frac{1}{\varepsilon_{\rm CT}}$$
(20)

$$\frac{[D]_0[A]_0}{A} = \frac{1}{K_{\text{CT}}\varepsilon_{\text{CT}}} + \frac{[D]_0 + [A]_o}{\varepsilon_{\text{CT}}} - \frac{[C]}{\varepsilon_{\text{CT}}}$$
(21)

where A is the absorbance of the CT mixture $[D]_0$ and $[A]_0$ are the initial concentrations of the donor and acceptor respectively, and [C] represents the concentration of the CT complex.

The obtained low values of the formation constant (K_{CT}), listed in Table 1, indicates that the CT complex (T2T-2H·DDQH₂) has a low stability; i.e., weak CT complex, and this CT complex might be classified as a one of the contact-type charge-transfer complexes [26] in which the CT interaction results during random encounters whenever the donor (T2T-2H) and the acceptor $(DDQH_2)$ molecules are sufficiently close to one another. The computed K_{CT} values of (T2T-2H-DDQH₂) CT complex (Table 1) at different temperatures were utilized to determine the enthalpy change (ΔH) of this complex by using a Van't Hoff plot [25]. Gibbs free energy change (ΔG) was calculated from the equation: $\Delta G = -RT \ln K_{CT}$. The obtained results of the thermodynamic parameters are listed in Table 1. The data listed in Table 1 reveal that the formed CT complexes are better stabilized as the temperature is increasing. This indicates the endothermic nature of the (T2T-2H/DDQH₂) CT complex. Moreover, the high value of ΔS (cf. Table 1) indicates the random encounters of the two reacting species (T2T-2H and DDQH₂) characterizing to the contact-type CT complex interactions [26]. This could be supported by the determined Mulliken's ratio $(b/a)^2$, using the proposed relation [47,48] $b^2/a^2 = -\Delta H/hv$. In this relation, hv is the energy of the absorption band of the complex, where *a* and *b* are the coefficients of the dative bond and the nonbonding wave functions ($\Psi_{D^+A^-}$ and Ψ_{D-A} , respectively) of that CT complex. The obtained ratios (b^2/a^2) herein are close to those of many CT complexes of weak strength [26].

The ionization potential (IP) of the T2T-2*H* donor has been estimated from the energy of the CT transition using the empirical relation of Alosi and Pignataro [49]. The calculated IP value of the donor, T2T-2*H* (IP = 10.1 eV, cf. Table 1) indicates that the compound T2T-2*H* is a CT donor of weak strength and the formed complex is of the contact-type CT complexes. This provides a further convincing evidence for the weak T2T-2*H*/DDQH₂ CT interaction.

It is worthy to mention that, on measuring the electronic absorption spectra of the T2T/DDQ mixture solutions in CHCl₃, the non-polar solvent, cf. Fig. 6, the obtained values of the formation constants, thermodynamic parameters and ionization potential are close to those obtained in the case of using MeOH as a solvent, cf. Table 1. This consistency of the T2T/DDQ interaction in case of using either CHCl₃ or MeOH as a solvent means that the T2T/DDQ redox reaction does not depend largely on the solvent polarity and, moreover, the probable interaction of DDQ and MeOH by themselves [50] is excluded too. Thus, methanolysis of DDQ by MeOH

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Table 1

Spectral characteristics, formation constants (K_{CT}), molar extinction coefficients (ε_{CT}), thermodynamic parameters, and (b^2/a^2) values for the CT T2T-2H-DDQH₂ molecular complex in a polar (MeOH) and a non-polar (CHCl₃) solvents at different temperatures and, as well as, the ionization potential of the donor.

Solvent	$\lambda_{max}\left(nm ight)$	IP (eV)	$K_{\rm CT}$ (dm ³ mol ⁻¹)				$\varepsilon_{\rm CT}$ at 20 °C (dm ³ mol ⁻¹ cm ⁻¹)	$-\Delta H^0$ (kJ mol ⁻¹)	$-\Delta S^0$ (J mol ⁻¹)	$-\Delta G^0 (\mathrm{kJmol^{-1}})$	(b^2/a^2)
			10°C	15°C	20°C	25 °C					
CHCl ₃	350	10.1	25.41	-	45.61	56.13	5105.2	37.55	159.67	9.98	0.11
MeOH	350	10.1	-	10.87	24.78	36.27	49541.5	86.11	319.44	8.89	0.24



Fig. 6. Electronic absorption spectra of (T2T–DDQ) mixture solutions in CHCl₃ at 25 °C. ([DDQ]= 2.0×10^{-4} mol dm⁻³ (constant), [T2T]=(a) 2.0×10^{-3} mol dm⁻³, (b) 1.8×10^{-3} mol dm⁻³, (c) 1.6×10^{-3} mol dm⁻³, (d) 1.4×10^{-3} mol dm⁻³, (e) 1.2×10^{-3} mol dm⁻³, (f) 1.0×10^{-3} mol dm⁻³, (g) 0.8×10^{-3} mol dm⁻³, (h) 0.6×10^{-3} mol dm⁻³, (i) 0.4×10^{-3} mol dm⁻³, and (j) 0.2×10^{-3} mol dm⁻³). The spectra have been measured after elapsing 60 min of mixing the reactants.

(interaction of DDQ and MeOH by themselves) is well known [50], however, this interaction is characterized by two remarkable observations: it occurs in a period of 48 h [50], and, in addition, one of the DDQ/MeOH reaction intermediates has a visible absorption spectral band at 465 nm [50]. None of these observations has been seen, herein in our case, for the interaction of T2T/DDQ in presence of MeOH as a solvent.

Thus, except the lapse of time required to reach the maximum intensity of the CT band, the solvent polarity has no effect on the T2T-2*H*/DDQH₂ CT complex formation. This means that the formed CT complex does not have a dative structure (i.e., the CT complex does not exist in the dative $D^+ \cdot A^-$ inner sphere). The CT complex (T2T-2*H*·DDQH₂) exists, then, in the neutral species (D and A) having the structure of the nonbonding outer sphere (i.e., D·A outer sphere) which gives a supporting evidence for the weak strength of both the new donor (T2T-2*H*) and the new acceptor (DDQH₂), resulting in situ through the T2T/DDQ interaction.

4. Conclusions

The T2T–DDQ system has performed multiple interactions: Two charge transfer interactions and a redox reaction. A first CT interaction has been occurred between T2T and DDQ. This interaction has led to a redox reaction resulting in dehydrogenation of T2T to the corresponding T2T-2*H*, whereas DDQ is reduced to the corresponding hydroquinone (DDQH₂). However, this redox reaction is not the terminal outcome of the interacting system T2T–DDQ. A second CT interaction has been occurred between the two species resulting in situ; the oxidized form (T2T-2*H*) as a new donor and the reduced form (DDQH₂) as an unconventional new acceptor. The product (T2T-2*H*·DDQH₂) is a CT complex of the contact-type CT complexes characterizing by the low formation constants and low stability that readily breaks down in polar solvents to its interacting species.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.04.078.

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