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Charge-Transfer Molecular Complexes of Guanazole and Some 1,2,4-Triazoles with σ- and π-Acceptors Involving a New Acceptor: Resulting In Situ; $DDQH_2$

Usama Mohamed Rabie,* Hasan Mahmoud Ali Salman,
and Moustafa Hassan Mohamed Abou-El-Wafa

Chemistry Department, Faculty of Science at Qena, South Valley University, Qena 83523, Egypt

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Charge-transfer complexes of 1,2,4-triazole (1T), 3-amino-1,2,4-triazole (2T), 4-amino-4*H*-1,2,4-triazole (3T), and guanazole (3,5-diamino-1,2,4-triazole) (4T) with iodine as a typical σ-type acceptor and with typical π-type acceptors (tetracyanoethene (TCNE) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)) have been synthesized and characterized. The spectral characteristics and thermodynamic properties of such CT complexes were investigated. The system triazoles/iodine is characterized by the formation of triiodide ions (I_3^-), which is proposed to occur via the initial formation of outer-sphere charge-transfer complexes. The systems (1T–4T)/TCNE and (1T–4T)/DDQ produced the corresponding anion radicals, $TCNE^{\bullet-}$ and $DDQ^{\bullet-}$, respectively. The time dependency of the spectral bands due to the 4T/TCNE system is discussed in terms of the scope of transformation from outer-sphere CT complexes to inner-sphere ones. Meanwhile, for the system 4T/DDQ the time dependency is accounted for by the stepwise reduction of DDQ to its anion radicals, and then to the corresponding hydroquinone (2,3-dichloro-5,6-dicyanohydroquinone), $DDQH_2$. However, because the resulting in situ ($DDQH_2$) was an unconventional new acceptor, it formed a CT complex with the donor (4T). The results show that the formed complexes are strong kinds of n–σ and n–π types in a 1:2 and 1:1 stoichiometry for the complexes of triazoles donors with iodine and DDQ, respectively.

1,2,4-Triazoles have found applications as plasticizers and adhesives, and in the photographic industry,[1] and have shown much importance in pharmaceutical industries,[2,3] where they are used in the production of fungicides, herbicides, and drugs. Pharmaceutical compounds containing triazole derivatives inhibit the growth of tumors and cancer in mammals, and are also used to treat viral infections.[4] They also have antibacterial activity.[5] Their n-electrons and the not extended conjugated π-electron system have attracted many researchers for extensive studies. Growing interest in the charge-transfer interaction stimulated the present work. Charge-transfer (CT) complexes of nitrogen heterocyclic compounds with iodine are known to occur by using nonbonding electrons on the nitrogen atom(s).[6–8] In this study, 1,2,4-triazole and some of its different derivatives were selected to ascertain the role of different groups on the triazole moiety through the interaction with iodine (I_2) as a typical σ-acceptor and with tetracyanoethene (TCNE) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as representative π-acceptors. During the course of our own work, we found that CT complexes can, indeed, undergo outer-sphere charge transfer to give $D \cdot A$ adducts, and then undergo complete electron transfer to give the $D^+ A^-$ salts (dative structures). Herein, we are the first to show that the hydroquinone $DDQH_2$ resulting, in situ, from the CT interaction of DDQ with 4T can also interact as a π-acceptor with the same donor (4T) to yield a new CT complex. Understanding and controlling such a point of view might have useful applications. A reinvestigation of many previous studies have shown a time dependency of DDQ interactions with strong donors.

Experimental

Materials and Solutions. The donors, triazoles, were purchased from Aldrich Chemical Co. and were used without further purification. The electron acceptors, TCNE and DDQ (Aldrich Co.), were recrystallized from chlorobenzene and dry dichloromethane, respectively, whereas iodine (E. Merck AG) was resublimed under reduced pressure. Hydroquinone ($DDQH_2$) was prepared according to a prior route.[9] The solvents used were of spectral pure grade (BDH).

Physical Measurements. The electronic absorption spectra were recorded on a Perkin-Elmer Lambda 40 spectrophotometer equipped with a Julabo FP 40 thermostat (±0.1 °C) using 1.0 cm matched quartz cells. IR spectra of the synthesized solid CT complexes were recorded on a Shimadzu IR-408 spectrophotometer. Computations were performed while making use of both Benesi–Hildebrand[10] and Scott[11] methods with the aid of two programs based on unweighted linear least-squares fits. The thermodynamics was obtained by means of a computer program based on van't Hoff plots.[12] Due to the sparingly soluble character of the donors (2T–4T) in nonpolar solvents (viz, chloroform, dichloromethane, and 1,2-dichloroethane), all spectral measurements were carried out in methanol. Stock solutions of the donors or acceptors were prepared in methanol, where they were freshly prepared prior to use. Elemental analyses for the C, H, and N contents of the prepared solid complexes were carried out at the microanalytical laboratory, Cairo University, Cairo, Egypt. The Cl and I contents were estimated by making use of conventional methods.

Synthesis of Solid CT Complexes. 1:2 (donor:acceptor) solid CT complexes of iodine with each of the donors (1T–4T) were synthesized by mixing a methanolic solution of I_2 (4.0 mmol) with that

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of the donor (2.0 mmol for each). The resulting complex solutions were left overnight at room temperature. The solid complexes were separated as fine crystals. On the other hand, solid 1:1 CT complexes of the donors (1T–4T) with DDQ were prepared by mixing the required amount of each of the donors dissolved in the least amount of methanol with an appropriate amount of the acceptor in a 1:1 molar ratio. The mixture solutions were refluxed for 0.5–1.5 h. The solid products were separated out by cooling the solutions, and washed several times with methanol. In all cases, the precipitates were collected and recrystallized from absolute ethanol and dried. The found values of the elemental analysis were in satisfactory agreement with the calculated values.

(1T–I_2) Complex.- Found: C, 4.23; H, 0.10; N, 7.35; I, 87.92%. Calcd for $C_2H_3N_3I_4$: C, 4.17; H, 0.05; N, 7.29, I, 88.02%.

(2T–I_2) Complex.- Found: C, 4.13; H, 0.11; N, 9.48; I, 85.81%. Calcd for $C_2H_4N_4I_4$: C, 4.06; H, 0.07; N, 9.47; I, 85.79%.

(3T–I_2) Complex.- Found: C, 4.05; H, 0.08; N, 9.44; I, 85.76%. Calcd for $C_2H_4N_4I_4$: C, 4.06; H, 0.07; N, 9.47; I, 85.79%.

(4T–I_2) Complex.- Found: C, 4.00; H, 0.09; N, 11.55; I, 83.68%. Calcd for $C_2H_5N_5I_4$: C, 3.96; H, 0.08; N, 11.54; I, 83.66%.

(1T–DDQ) Complex.- Found: C, 40.53; H, 1.09; N, 23.75; Cl, 24.05%. Calcd for $C_{10}H_3N_5O_2Cl_2$: C, 40.57; H, 1.02; N, 23.65; Cl, 23.96%.

(2T–DDQ) Complex.- Found: C, 38.55; H, 1.30; N, 27.10; Cl, 22.68%. Calcd for $C_{10}H_4N_6O_2Cl_2$: C, 38.61; H, 1.31; N, 27.02; Cl, 22.79%.

(3T–DDQ) Complex.- Found: C, 38.53; H, 1.28; N, 26.97; Cl, 22.78%. Calcd for $C_{10}H_4N_6O_2Cl_2$: C, 38.61; H, 1.31; N, 27.02; Cl, 22.79%.

(4T–DDQ) Complex.- Found: C, 36.62; H, 2.18; N, 29.85; Cl, 21.55%. Calcd for $C_{10}H_7N_7O_2Cl_2$: C, 36.61; H, 2.15; N, 29.88; Cl, 21.61%.

Attempts to prepare solid CT complexes of the donors (1T–4T) with TCNE have so far been unsuccessful.

Results and Discussion

Spectral Characteristics of the CT Complexes between 1,2,4-Triazoles and I_2. Electronic absorption spectra of the MeOH solution mixtures of the studied triazoles (1T–4T) with I_2 were recorded in the wavelength range 250–600 nm. Methanol was used as a blank because none of the reacting species has any absorption band(s) that can perturb the spectra of the CT mixture solutions. The reaction of the triazoles (1T–4T) with I_2 in MeOH always led to the formation of salts via electron transfer. All attempts to identify the charge-transfer band(s) for mixtures of triazoles and I_2 in MeOH failed. Instead, the characteristic bands[13–15] of the triiodide ion (I_3^-) at 292 and 363 nm grew in (Fig. 1 curve a). The electronic spectra of the redissolved solid complexes in MeOH indicate the presence of I_3^- ions.[13–15] Moreover, the formed solid CT complexes of (1T–4T) donors with I_2 have the 1:2 stoichiometric ratio, as indicated by the elemental analytical data, i.e., $D^+I\cdot I_3^-$.

Early evidence was reported[6,16] for a transformation of the associative outer complexes to the dissociative inner complexes. The only reaction pathway previously reported[17–19] for triiodide formation via an interaction of the σ-acceptor iodine with strong donors is:

$$\underset{\text{donor}}{D} + \underset{\text{acceptor}}{I_2} \rightarrow \underset{\text{outer sphere}}{DI_2} \rightleftharpoons \underset{\text{inner sphere}}{DI\cdot I} \tag{1}$$

$$DI\cdot I + I_2 \rightleftharpoons D^+I\cdot I_3^- \quad \text{(triiodide complex)} \tag{2}$$

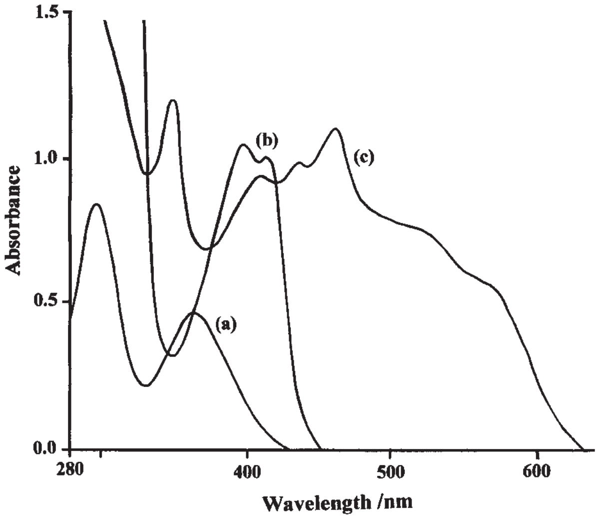


Fig. 1. Electronic absorption spectra of the methanolic CT mixture solutions of 2T with I_2, TCNE, and DDQ at 25 °C. a) 1.6×10^{-2} mol dm^{-3} 2T + 2.0×10^{-4} mol dm^{-3} I_2. b) 2.8×10^{-2} mol dm^{-3} 2T + 4.0×10^{-3} mol dm^{-3} TCNE. c) 8.0×10^{-2} mol dm^{-3} 2T + 4.0×10^{-4} mol dm^{-3} DDQ.

Thus, a lone pair of electrons present on each of the nitrogen atoms of the triazoles emphasizes this interaction pathway.

UV–Vis Study of CT Complexes between 1,2,4-Triazoles and TCNE. Electronic absorption spectra obtained for methanolic CT complex solutions of the (1T–3T)/TCNE showed two main absorption bands located at 390–8 and 410–4 nm. A representative spectrum is shown in Fig. 1 (curve b) of the (2T/TCNE) CT mixture solution. These spectroscopic features could be explained based on the fact that the formed (1T–3T)/TCNE complexes are of the strong type. Thus, these CT complexes dissociated first into the corresponding radical donor cations and anions, $TCNE^-$, then the $TCNE^-$ anions were reduced (base hydrolysis) into 1,1,2,3,3-pentacyanopropenide ions,[20] $PCNP^-$, as a result of the basicity of the triazole donors and the presence of methanol (protic solvent). Accordingly, the two bands that appeared at 390–8 and 410–4 nm could be assigned to the absorption of $PCNP^-$.[21,22] Thus, the recorded spectra of these complexes are perturbed by those of the radical anions; they do not exhibit well-defined CT band(s), and all attempts to obtain definite CT band(s) did not succeed. Thus, the determination of the formation constants of these CT complexes is not possible.

Donor 4T has a unique interaction behavior with the acceptor, TCNE. The electronic absorption spectra of the mixture 4T/TCNE in methanol (Fig. 2) showed four main bands, that were neither simultaneously increasing nor decreasing. The shorter wavelength band at 378 nm was decreasing with time until it completely vanished after 15 min, while two other bands at 396 and 415 nm appeared and reached more or less constant absorbance values during the same period of time. Meanwhile, the longer wavelength band at 450sh nm was time independent. Because the shorter band at 378 nm could be ascribed as a CT band between the donor 4T and the TCNE acceptor, the longer one at 450sh nm could also be assigned as another CT band from another site of the triazole moiety. However, the two re-

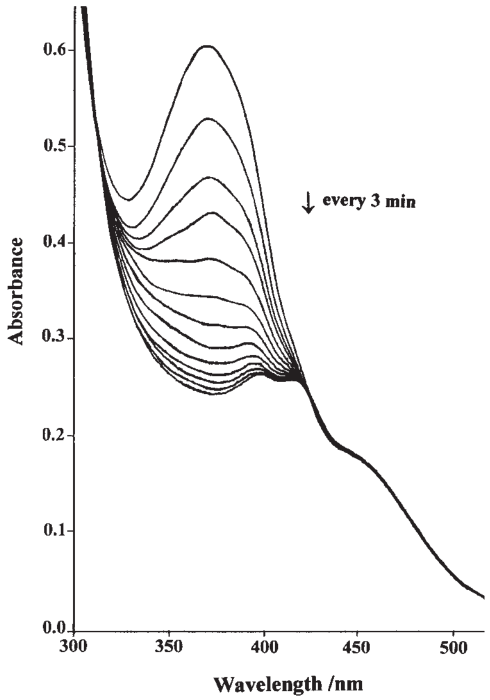
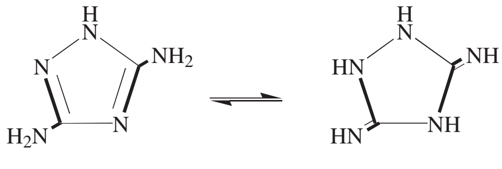


Fig. 2. Electronic absorption spectra of the methanolic (4T–TCNE) mixture solution at 25 °C. ([4T] = 2.4×10^{-2} mol dm^{-3} and [TCNE] = 2.0×10^{-3} mol dm^{-3}).

maining bands at 396 and 415 nm are well known to refer to the anion radicals (TCNE$^-$).[21,22] Thus, one can ascribe the observed two absorption bands at 378 and 450sh nm as a doublet CT transition of the n–π type for one molecular complex. Thus, this CT complex dissociates into the cation 4T$^+$ and anion radicals (TCNE$^-$). This indicates that two of the nitrogen atoms of the donor 4T share in the CT interaction with TCNE to perform these two transitions characterized by the two bands at 378 and 450sh nm to the lowest unoccupied molecular orbital (LUMO) of TCNE and TCNE$^-$, respectively.

The amazing unique behavior of compound 4T (guanazole) may refer to its capability to undergo tautomerism or mesomerism (Scheme 1),[23] whereas the resulting two imino (**I**) groups could be the charge or electron-donating sites. A failure to isolate any of the (1T–3T)/TCNE or even 4T/TCNE solid complexes makes it is impossible to investigate and characterize these interactions any further.

Under the conditions [4T] $\gg$ [TCNE] and no delay in time to avoid the formation of the anion radical TCNE$^-$, the electronic absorption spectra of the methanolic CT mixture solutions of 4T as a donor with the acceptor TCNE were measured. The absorbance values obtained from the CT band at $\lambda_{\max} = 378$ nm at different temperatures (10, 15, 20, and 25 °C) were used to determine the formation constants (K_{CT}) and the molar extinction coefficients ($\varepsilon_{\mathrm{CT}}$) of the CT complex (4T–TCNE), while making use of the Benesi–Hildebrand[10] and Scott[11] equations. The obtained high K_{CT} (Table 1) values of the 4T–TCNE CT complex suggest that such a complex is one of the strong n–π types. The computed K_{CT} values for a series of temperatures (10–25 °C) were utilized to determine the enthalpy change (ΔH) of CT complex formation using van't Hoff plots[12] ($R \ln K_{\mathrm{CT}} = -\Delta H/T + \Delta S$). The obtained ΔH value (Table 1) reflects that the interaction of the donor 4T with the TCNE acceptor is exothermic, in agreement with the deduced high formation constants of the formed complex (4T/TCNE). Mulliken's ratio, $(b/a)^2$, was estimated by using the proposed relation,[24] $b^2/a^2 = -\Delta H/h\nu$, where a and b are the coefficients of the dative bond and the nonbond wave functions ($\Psi_{\mathrm{D^+A^-}}$ and $\Psi_{\mathrm{D\text{-}A}}$, respectively) of the CT complex. The value found is comparable to those previously seen[24–26] for cases with strong CT complexation.



(I) **(II)**

Scheme 1.

The ionization potential (IP) of the highest filled molecular orbital on guanazole (4T) has been estimated from the energy of the CT transition using an empirical relation of Aloisi and Pignataro.[27] The obtained value of the ionization potential of the 4T donor (9.58 eV, cf. Table 1) is higher than those of amines,[28] but compares with those of imine[29] compounds. Thus, one can deduce that the donor 4T is mainly in the imine form (**II**) (Scheme 1), one of the strong donors.

Spectral Characteristics of the CT Complexes between 1,2,4-Triazoles and DDQ. Generally, when using DDQ as an electron acceptor, each of the triazoles donors (1T–4T) has its own unique story. The recorded spectra for the methanolic CT complex solutions of the donors (1T–3T) with DDQ displayed a series of absorption bands at $\lambda_{\max} = 346$–8, 410–2, 438, 462, 520–6, 566–8 nm (cf. Fig. 1 curve c). These bands are characteristic to the anion radicals (DDQ$^{\bullet-}$) from the peak positions and shapes.[30–32] This means that complexes of these triazoles with DDQ exist in solutions predominately in the dissociated state: radical cations and anions, D$^+$ A$^-$. The appear-

Table 1. Spectral Characteristics, Formation Constants (K_{CT}), Molar Extinction Coefficient ($\varepsilon_{\mathrm{CT}}$), Thermodynamic Parameters, and $(b/a)^2$ Values for CT Molecular Complexes of 3,5-Diamino-1,2,4-triazole with the π-Acceptors at Different Temperatures in Methanol as well as the Ionization Potentials of the Donor (4T)

Electron acceptor	$\lambda_{\max}$ /nm	E_{CT} /eV	IP /eV	K_{CT}/dm^3 mol^{-1} 10	15	20	25	$\varepsilon_{\mathrm{CT}}$ at 20 °C /dm^3 mol^{-1} cm^{-1}	$-\Delta H^\circ$ /kJ mol^{-1}	$(b/a)^2$
TCNE	378	3.27	9.58	174.7 ±2.11	158.7 ±1.94	145.4 ±1.89	130.9 ±1.73	274.40 ±3.79	13.4 ±0.15	0.04
DDQH$_2$	400	3.09		1279.32 ±19.20	1244.24 ±17.42	1209.61 ±17.54	1167.08 ±16.33	4415.18 ±49.52	5.04 ±0.09	0.01

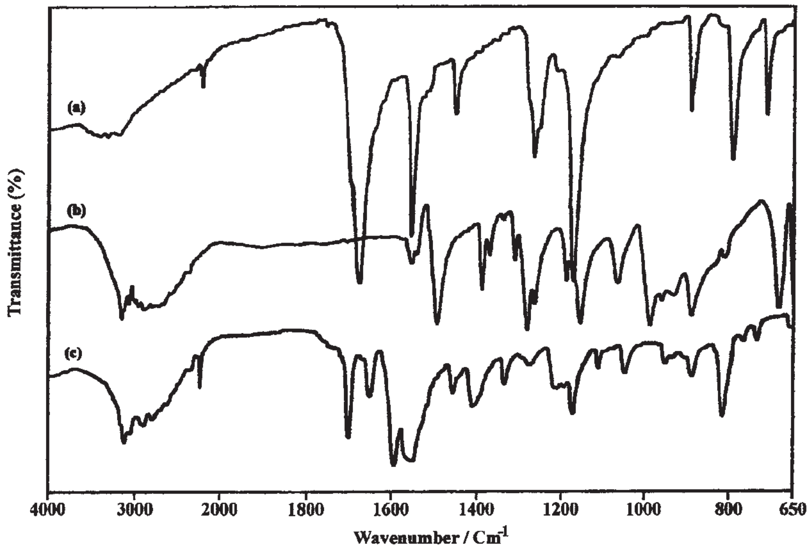


Fig. 3. Infrared spectra of the 1T–DDQ CT complex. a) IR spectrum of the free DDQ. b) IR spectrum of the free donor (1T). c) IR spectrum of the CT complex.

ance of structural bands characterizing the DDQ$^{\bullet-}$ anion radicals seems to follow the previously reported[29] interaction pathway. Thus, it can probably be ascribed to a transformation of the CT complex from an outer-sphere type D–A, a nonbonding structure, to an inner-sphere complex, D^{+}–A^{-}, a dative structure. Thus, an equilibrium dissociation to the radicals D^{+} and A^{-} is established in the ground state:

$$\mathrm{D} + \mathrm{A} \rightarrow \mathrm{D}^{+}\text{–}\mathrm{A}^{-} \rightleftharpoons \mathrm{D}^{+} + \mathrm{A}^{-}$$

Due to the fact that the recorded spectra of these complexes are perturbed by those of the radical anions, they do not exhibit well-defined CT band(s). All attempts to obtain a definite CT band(s) did not succeed and, in turn, determining the formation constants of these CT complexes is not possible.

A careful examination of the IR spectra of the solid complexes formed by each of the triazole (1T–3T) donors with DDQ gives evidence[32] that the structures of these complexes could be represented by (1T–DDQ$^{\bullet-}$), (3T–DDQ^{2-}), and (2T–DDQH^{-}). This indicates the different behaviors in the interaction of the studied donors (1T–3T) with the acceptor, DDQ. A comparison of the important IR spectral bands of the free donors (1T–3T) and those of the π-acceptor DDQ with the corresponding ones appearing in the IR spectra of the CT complexes (cf. Fig. 3, a representative example) shows a strong pattern due to different anions:[32] DDQ$^{\bullet-}$, DDQ^{2-} and DDQH^{-} of DDQ complexes with donors 1T, 3T, and 2T, respectively. Namely, the vibrational frequencies of the C≡N groups for the free DDQ observed at 2250 cm^{-1} is shifted to 2214–20 cm^{-1} in the corresponding IR spectra of all CT complexes with DDQ. The group bands connected to C–Cl vibrations, which appeared at 802 and 722 cm^{-1} in the IR spectra of free DDQ, exhibit a shift to lower frequencies in the corresponding IR spectra of the CT complexes (at 750–55 and 700–10 cm^{-1}). The dramatic differences arise from the band characteristics to the stretching vibrations of the C=O groups (at 1668 cm^{-1} for free DDQ). For the CT complex of DDQ with 1T, this band split and shifted to 1650 and 1700 cm^{-1}. However, for the (3T–DDQ^{2-}) complex, the corresponding band appeared at 1560 cm^{-1} characteristic[33] to DDQ^{2-}. Meanwhile, the anion DDQH^{-} of the complex resulting from 2T with DDQ was indicated by two characteristic bands[32,33] in the IR spectra of the complex (at 3380 cm^{-1} for the OH group and 1570 cm^{-1} for the CO group). An elemental analysis of the formed CT complexes between the triazoles donors (1T–3T) with DDQ indicates, and may even agree with, our suggestion.

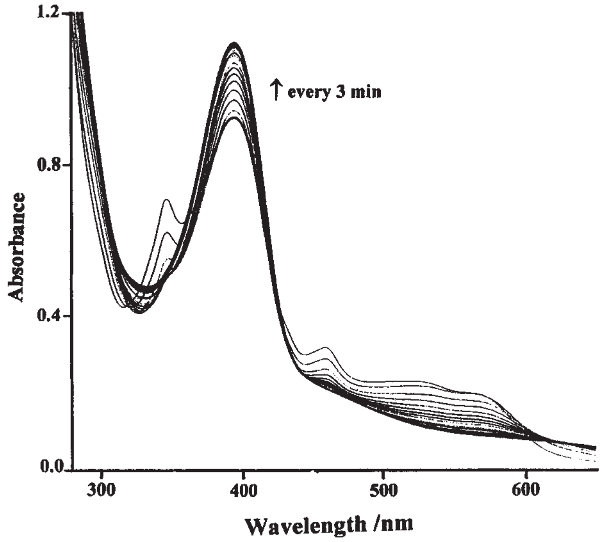


Fig. 4. Electronic absorption spectra of the CT complex between 4T and DDQ in MeOH at 25 °C. ([4T] = 8.0×10^{-3} mol dm^{-3} and [DDQ] = 2.0×10^{-4} mol dm^{-3}).

Also, the amazing behavior is attained from the donor guanazole (4T) through its interaction with the π-acceptor, DDQ. The electronic absorption spectra of methanolic CT complex solutions of 4T with DDQ in the wavelength range 300–700 nm displayed the structural characteristic[30–32] bands to the anion radicals, DDQ$^{\bullet-}$. Surprisingly, these bands were time dependent. Within a period of 45 min, these bands decreased until they completely vanished, meanwhile, a new band at 400 nm increased (Fig. 4). The new band (at $\lambda_{\max} = 400$ nm) reached its maximum intensity within 45 min.

This band could be assigned as a CT band arising from charge transfer from the highest occupied molecular orbital (HOMO) of the 4T donor to the lowest unoccupied molecular orbital (LUMO) of the resulting new acceptor, $DDQH_2$. It was previously reported[34] that the reduced hydroquinone ($CHLH_2$) resulting during the interaction of *p*-chloranil (CHL) can also interact as a π-acceptor. However, the slow formation and stabilization of the UV–visible CHL CT band could be explained by the first reduction of CHL to $CHLH_2$. Herein, we assumed that DDQ followed CHL in forming the corresponding hydroquinone. Much evidence is presented hereafter to enhance our suggestion that the reduction of DDQ to $DDQH_2$ can account for the time dependency (45 min). The resulting, in situ, hydroquinone ($DDQH_2$) reacted as a CT π-acceptor with the donor 4T. First, we agree[35,36] that the only rout to obtain the anion radicals ($DDQ^{\bullet-}$) is the first formation of the CT complex between 4T and DDQ. This complex then dissociates to the corresponding dative structure, consisting of the cation ($4T^{+}$) and the anion ($DDQ^{\bullet-}$): (4T + DDQ → 4T•DDQ *outer sphere CT complex* → $4T^{+}\bullet DDQ^{\bullet-}$ *inner sphere* (dative structure)), i.e., the first recognized structural bands. Second, the formed $DDQ^{\bullet-}$ has only two routes: either a chemical reaction with the 4T or to be reduced to the corresponding hydroquinone ($DDQH_2$).

We believe that no chemical reaction was occurred, but, suggest instead, that DDQ was reduced to $DDQH_2$ ($DDQ^{\bullet-}$ (anion radicals) $+ H^{+} \rightarrow DDQH_2$) using protons coming from the solvent, methanol, or actually and particularly from the donor 4T, because we worked with an excess donor (4T). Further, a CT interaction between the donor 4T and the resulting new acceptor, $DDQH_2$ has occurred. In what follows some evidence is mentioned to confirm our assumptions: 1) The appearance of only one band (at $\lambda_{max} = 400$ nm) characterized by a constant absorbance value indicates the existence of one species. 2) This band (at $\lambda_{max} = 400$ nm) is not due to the absorption of any of the following species: 4T, DDQ, $DDQ^{\bullet-}$, or $DDQH_2$ (previously prepared).[9] 3) The same band (at $\lambda_{max} = 400$ nm) was also displayed in the electronic absorption spectra of the methanolic mixture solution of 4T with $DDQH_2$. 4) The electronic spectra of the redissolved solid complex in methanol displayed the same band (at $\lambda_{max} = 400$ nm). 5) An elemental analysis of the solid complex indicated the formation of 4T:$DDQH_2$ with the stoichiometry 1:1. 6) The capability of 4T to ascertain tautomerism (Scheme 1) and, in turn, the occurrence in the imino (**I**) form[23] shows that it has a unique and different behavior composed to the other studied triazoles (1T–3T).

Also, 7) important evidence arose by comparing the important IR spectral bands of the free donor (4T), free DDQ and free $DDQH_2$ with the corresponding ones that appeared in the IR spectra of the obtained CT complex. Except for some reasonable shift of the functional bands of both the 4T donor and the $DDQH_2$ acceptor, the IR spectrum of the 4T–$DDQH_2$ CT complex seems to be a superposition of the individual IR spectrum of 4T and $DDQH_2$. The most remarkable and interesting observation concerning the IR spectra of the (4T/DDQ) CT complex is the disappearance of the 1668 cm^{-1} band characteristics to the stretching vibrations of CO for free DDQ, whereas, instead, the band assigned to OH*s* appears at the wavelength 3305 cm^{-1}. Thus, one can suggest that the two components forming the solid CT complex are 4T, or particularly $4T^{+}$, as the donor, and the unconventional acceptor $DDQH_2$.

For determining the formation constants (K_{CT}) and molar extinction coefficients (ε_{CT}) of the CT complex (4T–$DDQH_2$), the electronic absorption spectra of the 4T–DDQ methanolic mixture solutions were measured after 45 minutes of mixing, whereas the absorbance values were obtained from the CT band located at $\lambda_{max} = 400$ nm. The obtained high values of K_{CT} (Table 1) indicate the high stability of the CT complex ($4T\bullet DDQH_2$). The computed K_{CT} values of 4T/$DDQH_2$ (Table 1) were utilized to determine the enthalpy change (ΔH) of this complex by using a van't Hoff plot.[12] The obtained ΔH value (Table 1) reflects that the interaction of the donor 4T with the $DDQH_2$ acceptor is exothermic, in agreement with the deduced high formation constants of the formed complex (4T/$DDQH_2$). The estimated value of Mulliken's ratio, $(b/a)^2$, is comparable to those previously seen[24–26] for cases with strong CT complexation.

Conclusions

The interaction of heterocyclic species containing nitrogen atom(s) with σ- and π-acceptors is well known, but we show here that in a polar solvent, methanol, I_2/(1T–4T) triazoles forms the triiodide ions (I_3^{-}) via the formation of outer-sphere CT complexes. The π-acceptor (TCNE or DDQ)/triazoles (1T–3T) system forms corresponding radical anions ($TCNE^{\bullet-}$ and $DDQ^{\bullet-}$), and it is proposed that it occurs via prior CT complexation. The resulting $DDQH_2$ also interacts as an acceptor with the donor 4T to give the CT complex.

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