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Synthesis and Spectroscopic Characterization of Trazodone Charge Transfer Complexes with Different Types of π-Acceptors[1]

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Abstract—Charge transfer complexes (CTC) of trazodone hydrochloride (TZD) with picric acid (PA), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), tetracyanoquinodimethane (TCNQ), 2,6-dichloroquinone-4-chloroimide (DCQ), 2,6-dibromoquinone-4-chloroimide (DBQ), and *N*-bromosuccinimide (NBS) have been synthesized and studied using conductivity, UV-Vis, infrared, Raman and ^{1}H NMR spectroscopy. The stoichiometries of the complexes were found to be 1 : 1. Kinetic thermodynamic parameters (E^*, A, ΔS^*, ΔH^*, and ΔG^*) were also calculated using Coats–Redfern and Horowitz–Metzger equations.

Keywords: trazodone hydrochloride, charge transfer complexes, conductivity, TCNQ, DCQ, PA

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INTRODUCTION

Trazodone hydrochloride (TZD; Fig. 1) has been used as an antianxiety and sleep-inducing drug [1]. Its side-effect profile and potential toxicity were considerably different from those of the original antidepressants (i.e., the monoamine oxidase inhibitors [MAOIs] and tricyclic antidepressants [TCAs]) [2]. The primary use of trazodone was the treatment of major depression. Data from open and double-blind trials suggest the antidepressant efficacy of trazodone was comparable to that of amitriptyline, doxepin, and mianserin. Trazodone also showed anxiolytic properties, low cardiotoxicity, and relatively mild side effects [2].

Charge-transfer complexes are known to be involved in many chemical reactions like addition, condensation and substitution [3, 4]. Electron donor-acceptor CT-interactions play an important role in non-linear optical materials [5–8], drug-receptor binding mechanism [9], in solar energy storage [10] and in surface chemistry [11] as well as in many biological fields [12–14]. Charge-transfer complexes of organic species are intensively studied because of their special type of interaction, which is accompanied by transfer of an electron from the donor to the acceptor [15, 16]. The π–acceptors have numerous applications as analytical reagents, for example they have been used for the spectrophotometric determination of many drugs in pharmaceutical formulations [17–23]. In continuation of our studies on charge transfer complexes of dif-

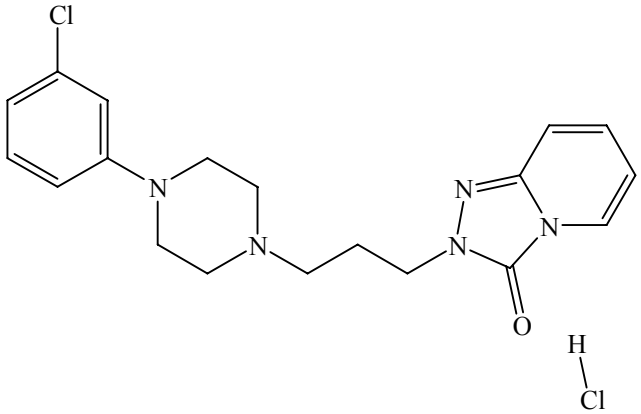

Fig. 1. Trazodone hydrochloride (TZD).

[1] The text was submitted by the authors in English.

ferent drug types[18, 19, 21–23], this paper discloses simple, fast, and accurate spectrophotometric method for the determination of trazodone using some π-acceptors.

EXPERIMENTAL

Trazondone hydrochloride was received from Egyptian International Pharmaceutical Industries Company EIPICO. Picric acid (PA), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), tetracyanoquinodimethane (TCNQ), 2,6-dichloroquinone-4-chloroimide (DCQ), 2,6-dibromoquinone-4-chloroimide (DBQ) and *N*-bromosuccinimide (NBS) were obtained from Aldrich and Fluka Chemical Companies. All chemicals were of analytical grade and were used without further purification.

Elemental analyses of carbon, hydrogen and nitrogen contents were performed using a Perkin Elmer CHN 2400 instrument. The molar conductivities of freshly prepared 1.0×10^{-3} M solutions in DMSO were measured using Jenway 4010 conductivity meter. The electronic absorption spectra of the resulted charge transfer complexes were recorded in methanol within 900–200 nm range using a Perkin-Elmer Precisely Lambda 25 UV-Vis double beam Spectrometer fitted with a quartz cell of 1.0 cm path length. Infrared spectra within the range of 4000–400 cm^{-1} for the free reactants and the resulted CT-complexes were recorded in KBr discs using a Shimadzu FT-IR Spectrometer with 30 scans and 2 cm^{-1} resolution, while Raman laser spectra were measured on a Bruker FT-Raman instrument with 50 mW laser. ^{1}H-NMR spectra were recorded in DMSO solutions on a Bruker 600 MHz spectrometer using TMS as an internal standard. DTG-TG thermograms were obtained on a Shimadzu TGA-50H instrument at heating rate of 30 deg min^{-1} under a nitrogen flow. Scanning electron microscopy (SEM) and Energy Dispersive X-ray Detection (EDX) images were taken using an Joel JSM-6390 with an accelerating voltage of 20 kV. X-ray diffraction patterns were recorded on a Bruker Advanced 8 X-ray powder diffraction device, target CuK_α radiation, step scan mode with step = 0.05° and counting time 3.0 s/step.

Synthesis of solid TZD charge transfer complexes. Six new solid TZD charge transfer complexes were prepared as a yellow, brownish red, green, brown, dark brown and white powders for the PA, DDQ, TCNQ, DCQ, DBQ, and NBS complexes, respectively, by mixing 1 mmol (0.410 g) of TZD hydrochloride in 20 mL of methanol with 1 mmol of each acceptor, dissolved in 20 mL of chloroform. All mixtures were stirred for 1 hour at room temperature and the solid products were filtered off, washed with minimum amount of chloroform and dried under vacuum over anhydrous $CaCl_2$.

Analytical data. **[(TZD)(PA)] (I).** M_w = 637.43. Calculated, %: C 47.11; H 4.11; N 17.58, Found, %: C 47.01; H 4.10; N 17.44. **[(TZD)(DDQ)] (II).** M_w = 637.34. Calculated, %: C 50.88; H 3.95; N 15.38, Found, %: C 50.39; H 3.90; N 13.21. **[(TZD)(TCNQ)] (III).** M_w = 616.54. Calculated, %: C 60.39; H 5.07; N 20.45. Found, %: C 60.18; H 4.96; N 20.33. **[(TZD)·(DCQ)] (IV).** M_w = 618.77. Calculated, %: C 48.53; H 4.07; N 13.58. Found, %: C 48.43; H 4.02; N 13.21. **[(TZD)(DBQ)] (V).** M_w = 707.67. Calculated, %: C 42.43; H 3.56; N 11.88. Found, %: C 42.11; H 3.51; N 11.45. **[(TZD)(NBS)] (VI)**. M_w = 588.32. Calculated, %: C 46.95; H 4.97; N 14.28. Found, %: C 46.73; H 4.79; N 14.16.

RESULTS AND DISCUSSION

Electronic absorption spectra. Spectrophotometric titrations at 409, 465, 738, 338, 396, and 342 nm were performed (Fig. 2) for the reactions of TZD with PA, DDQ, TCNQ, DCQ, DBQ, and NBS, respectively. Absorbance of each charge transfer complexes was measured and plotted as a function of the $(C_a^0) : (C_d^0)$ ratio according to a known method [24]. To study solvent effect in a quantitative manner, the values of the equilibrium constant, K, the molar absorptivity ε, and the oscillator strength, *f*, of the TZD complexes have been calculated. The 1 : 1 modified Benesi–Hildebrand equation [25] was used in the calculations,

$$\frac{C_a^0 C_d^0 l}{A} = \frac{1}{K\varepsilon} + \frac{C_a^0 + C_d^0}{\varepsilon}, \quad (1)$$

where C_a^0 and C_d^0 are the initial concentrations of the acceptor and the donor TZD, respectively, and *A* is the absorbance of the charge transfer bands at 409, 475, 738, 338, 396, and 342 nm for PA, DDQ, TCNQ, DCQ, DBQ, and NBS, respectively. When the. $C_a^0 C_d^0/A$ values for each 1 : 1 charge transfer complex are plotted against the corresponding $C_a^0 + C_d^0$ values, straight lines are obtained with a slope of 1/ε and intercept of 1/*K*ε.

The physical spectroscopic data like formation constant (K_{CT}), molar extinction coefficient (ε_{CT}),

standard free energy (ΔG^0), oscillator strength (f), transition dipole moment (μ), resonance energy (R_N) and ionization potential (I_p) were calculated, and the different acceptors were found to have a pronounced effect towards the interaction with trazodone HCl. These calculations can be summarized as follows.

Oscillator strength. The oscillator strength f was obtained from the approximate formula [26].

$$f = (4.319 \times 10^{-9})\varepsilon_{max}\nu_{1/2}, \quad (2)$$

where $\nu_{1/2}$ is the band-width for half-intensity in cm^{-1} and ε_{max} is the maximum extinction coefficient of the CT-band. The oscillator strength values are given in Table 1. The data resulted reveal several points. The [(TZD)(A)] (where A= PA, DDQ, TCNQ, DCQ, DBQ, and NBS) charge transfer systems show high values of both formation constant (K) and molar absorptivity (ε). This high value of K reflects the high stability of the TZD charge transfer complexes as a result of the expected high rich donation of the TZD which contains five nitrogen atoms, ii) the different values of the oscillator strength, f, increases with increasing in the dielectric constant (D) of the solvent. This result could be explained on the basis of competitive solvent interactions with the acceptors [27, 28].

Transition dipole moment. The transition dipole moment (μ) of the TZD charge transfer complexes, have been calculated from the equation [29]:

$$\mu(\text{Debye}) = 0.0958[\varepsilon_{max}\nu_{1/2}/\nu_{max}]^{1/2}. \quad (3)$$

The transition dipole moment is useful for determining if transitions are allowed, that the transition from a bonding π orbital to an antibonding π* orbital is allowed because the integral defining the transition dipole moment is nonzero.

Ionization potential. The ionization potential (I_p) of the TZD charge transfer complexes were calculated using empirical equation derived by Aloisi and Piganatro [30, 31]:

$$I_p(\text{eV}) = 5.76 + 1.53\times 10^{-4}\nu_{CT}, \quad (4)$$

where ν_{CT} is the wavenumber in cm^{-1} corresponding to the charge transfer band formed from the interaction between donor and acceptor. The electron donating power of a donor molecule is measured by its ionization potential which is the energy required to remove an electron from the highest occupied molecular orbital.

Energy of the charge-transfer complexes. The energy of the charge-transfer complexes E_{CT} is calculated using the equation from [32];

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

where, λ_{CT} is the wavelength of the complexation band.

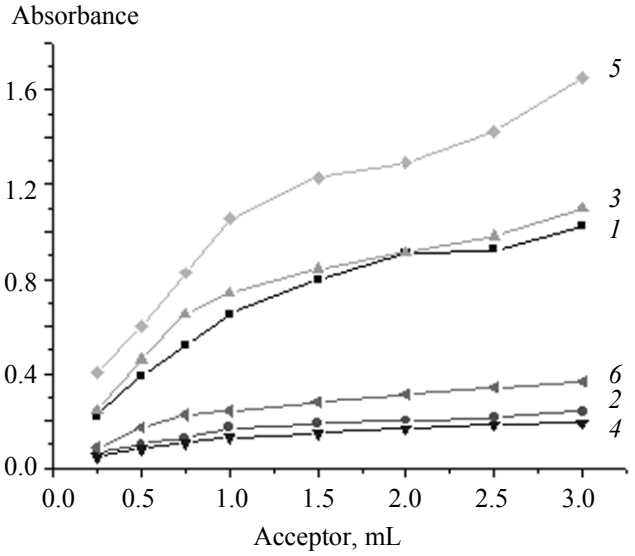

Fig. 2. Trazodone charge transfer complexes titration curves: (*1*) PA, (*2*) DDQ, (*3*) TCNQ, (*4*) DCQ, (*5*) DBQ, and (*6*) NBS.

Table 1. Spectroscopic data of TZD charge transfer systems

Complex	λ_{max}, nm	E_{CT}, eV	K, L/mol	ε_{max}, L mol^{-1} cm^{-1}	f	μ	I_p	R_N	ΔG^0 (25°C), J/mol
PA (**I**)	409	3.04	53463	29803	13	33	9.50	0.500	–26977
DDQ (**II**)	475	2.62	12381435	6206	2.68	16	8.98	0.165	–40470
TCNQ (**III**)	738	1.68	212296	29182	12	44	7.83	0.275	–30394
DCQ (**IV**)	338	3.68	203886	5231	2.26	13	10.28	0.202	–30294
DBQ (**V**)	396	3.14	84759	44291	19	40	9.62	0.600	–28119
NBS (**VI**)	342	3.64	1000000	9603	4.14	17	10.23	0.316	–34235

Resonance energy. Determination of resonance energy (R_N) [33] theoretically derived from the following equation:

$$\varepsilon_{max} = 7.7 \times 10^{-4}/(h\nu_{CT}/[R_N] - 3.5), \quad (6)$$

where ε_{max} is the molar absorptivity of the TZD charge transfer complexes at maximum CT band, ν_{CT} is the frequency of the CT peak and R_N is the resonance energy of the complex in the ground state.

Free energy. The standard free energy changes of complexation (ΔG^0) were calculated from the formation constants by the following formula [34]:

$$\Delta G^0 = -2.303RT\log K_{CT}, \quad (7)$$

Data from Table 1 reveal that the K values of charge transfer complexes with DDQ are higher than the corresponding values with PA, TCNQ, DCQ, DBQ, and NBS. This is consistent with the decrease in electron affinity of PA, TCNQ, DCQ, DBQ, and NBS relative to DDQ. On the other hand, the results indicate that the electron accepting ability of DDQ is higher than that of PA, TCNQ, DCQ, DBQ, and NBS. DDQ has four strong electron withdrawing groups (2CN and 2Cl) in conjugation with an aromatic ring which cause high delocalization leading to an increase in the Lewis acidity of the acceptor. The obtained results reveal that the CT complex formation process is exothermic and spontaneous. There is a good agreement with the literature values of the constants. When increasing electron affinity of acceptors, the values of the constants increases [35].

Infrared spectra. The infrared spectrum of free trazodone HCl has characteristic bands at 3000, 2954, 1704, 1650, 1600, 1350, and 750 cm^{-1} which are assigned to the stretching vibration bands of C–$H_{aromatic}$, C–$H_{aliphatic}$, C=O, C=N, C=C, C–N, and C–Cl, respectively. In the spectra of the TZD charge transfer complexes, each of them has characteristic bands for both the TZD donor and respective acceptor. These results confirmed and supported the association of the intermolecular charge transfer complexes between donor and acceptors. The small shifts in both band intensities and wavenumber values for both donor and acceptors in the TZD complexes compared to the free reactant molecules are due to the expected changes of molecular symmetries and electronic structures of the reactants upon complexation. For example, the ν(C=N) and ν(C=C) vibrations of free TZD are observed at 1650 and 1600 cm^{-1} but in case of PA charge transfer complex, these bands are shifted to lower wavenumbers at 1627 and 1553 cm^{-1}, respectively. This result confirms that intermolecular charge transfer complexation occurs via n–π* and π –π* as shown in Fig. 3a. The ν(C≡N) vibrations of DDQ and TCNQ alone are observed at 2223 and 2234 cm^{-1}, respectively. These vibrations occur at 2213 and 2228 cm^{-1} after complexation on the TZD–DDQ and TZD–TCNQ systems, respectively. The other changes are also observed for the ν(C=N) and ν(C=C) vibrations in case of TZD, these bands are shifted to 1643 and 1560 cm^{-1} and 1636 and 1537 cm^{-1}, respectively, upon complexation. These observations support the structures of TZD-DDQ and TZD–TCNQ charge transfer complexes as shown in Figs. 3b–3c. On the other hand, the ν(C=N) and ν(C=C) vibrations after complexation for the TZD-DCQ, TZD-DBQ, and TZD-NBS systems were shifted from 1650 to 1636–1643 cm^{-1} and from 1600 to 1590 cm^{-1}, respectively. These changes of the wavenumber values upon complexation are associated with the electron donation from TZD to the empty π* orbitals of acceptors (Figs. 3d–3f) [35]. The shift of the IR bands of the acceptor part to lower wavenumbers and those of the donor part to higher values reflects a donor to acceptor charge transfer of n–π* interaction, $D_{HOMO} \rightarrow D_{LUMO}$ transition [36].

Raman laser spectra. In the Raman laser spectra of the TZD charge transfer complexes, the main characteristic bands for both the donor and acceptor are presented in each case. These bands clearly confirm the charge transfer interactions between donor and acceptors. The Raman spectra are in a good agreement with infrared ones, the bands of the donor and acceptors in these complexes reveal small shifts in both band intensities and wavenumber values from those of the free components. This is due to the expected changes of electronic configuration of the reactants upon complexation. For example, the ν(C≡N) vibrations of free DDQ and TCNQ are observed at 2223 and 2234 cm^{-1}, respectively. These stretching vibrations occur at 2217 and 2225 cm^{-1} after complexation. Also, the other changes are observed for the ν(C=N) and ν(C=C) vibrations for each π-acceptors upon complexation. The ν(C=N) and ν(C=C) of free TZD is observed at 1650 and 1600 cm^{-1}, these bands are shifted to 1596–1640 and 1591–1541 cm^{-1} upon complexation. The changes of the wavenumber values upon complexation support the charge transfer associated with electron donor-acceptor donation from TZD to acceptors (PA, DDQ, TCNQ, DCQ, DBQ, and NBS).

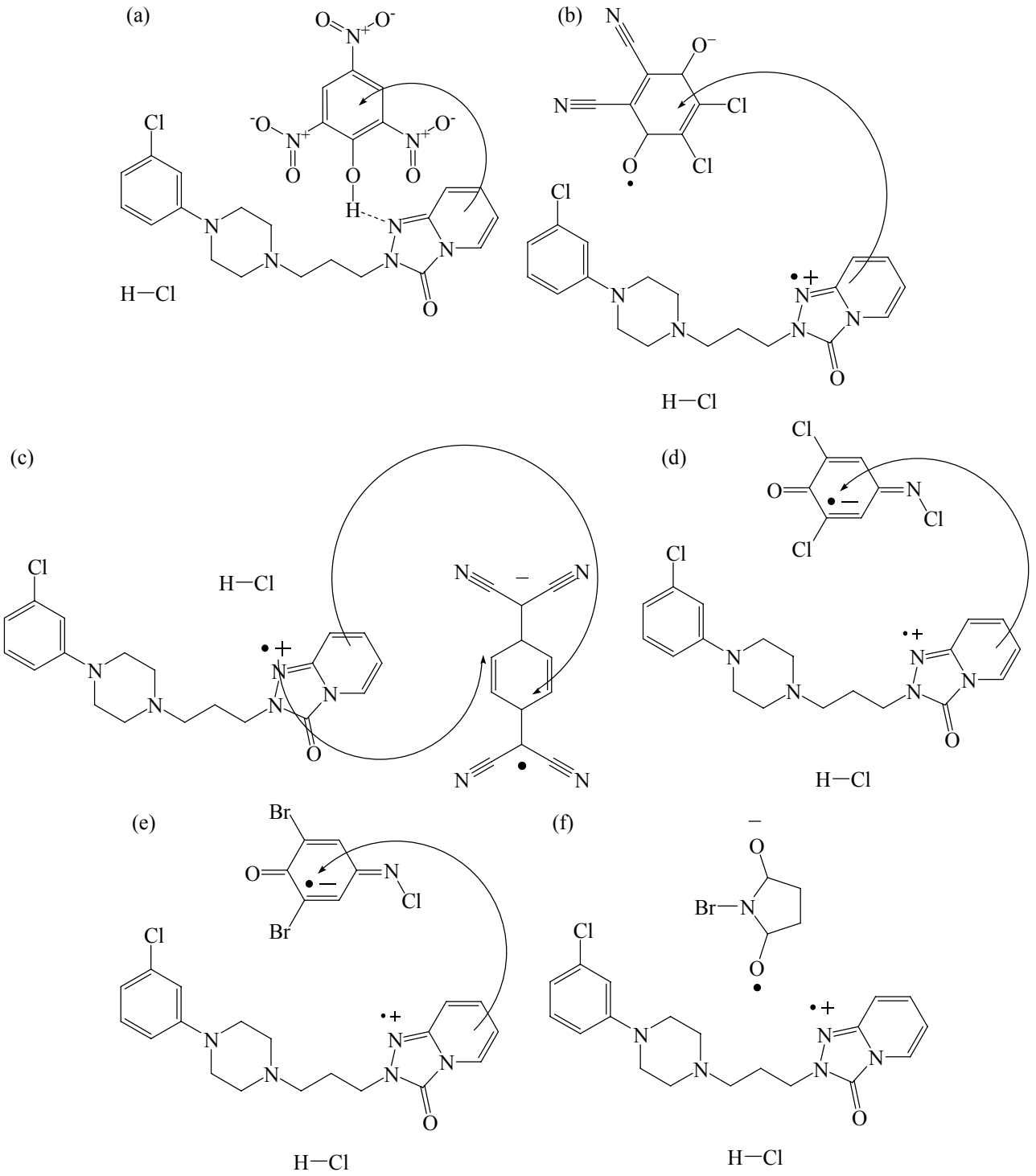

Fig. 3. Suggested structures of (a) PA, (b) DDQ, (c) TCNQ, (d) DCQ, (e) DBQ, and (f) NBS charge transfer complexes.

Proton NMR spectra. ^{1}H NMR spectrum of TZD HCl shows characteristic signals as: 2.16–2.12 m (2H), 2.64–2.60 t (2H), 2.73 s (4H), 3.09 s (4H), 4.12–4.07 t (2H), 6.51–6.46 m (1H, ArH), 7.02–6.93 m (2H, ArH), 7.09–7.08 d (2H, Ar H), 7.26–7.17 m (1H, ArH), 7.34–7.31 d (1H, ArH), 7.76–7.45 d (1H, ArH). In the ^{1}H NMR spectra of TZD-PA, TZD-DDQ, TZD–TCNQ, TZD–DCQ, TZD–DBQ, and TZD–NBS complexes,

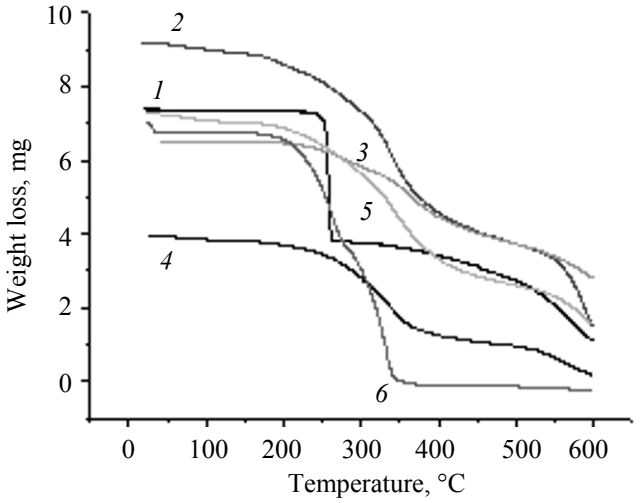

Fig. 4. TGA curves of (*1*) PA, (*2*) DDQ, (*3*) TCNQ, (*4*) DCQ, (*5*) DBQ, and (*6*) NBS charge transfer complexes.

the peaks of aromatic rings and methylene protons are shifted to higher ppm values which confirms clearly that charge transfer complexes were formed. During the complexation, charge transfer transitions occur with the excitation of an electron from HOMO of the donor to LUMO of the acceptor. The lowest energy of charge transfer transition will involve promotion of an electron residing in the high occupied molecular orbital (HOMO) of the donor to the acceptor. The interactions between TZD and π–acceptors give n–π* transitions and form radical ion pairs (radical cation $D^{+\cdot}$ and radical anions A^{-}). The conductivity of TZD in the presence of π-acceptors (PA, DDQ, TCNQ, DCQ, DBQ, and NBS) was measured and found to be slightly increased. This increasing in conductance after complexation supported that the charge transfer complex is formed from the formation of dative ion pairs [(TZD^{+})(Acceptor^{-})] complex.

XRD, SEM and EDX studies. Microstructure and morphology of the synthesized trazodone HCl charge transfer complexes were analyzed by electronic microscopy and XRD. From the recorded images, it can be observed that the TZD charge transfer complexes exist in the form of relatively crowded particles with various sizes. The X-ray powder diffraction revealed an amorpho-crystalline structures except for TZD-NBS with a good crystallinity. The qualitative highlighting of the constituents of each CT-complex was realized by EDX, based on the obtained spectra of the six π-acceptors, compared with the free dye spectrum. These data were corroborated with quantitative elemental analysis. It is worth to mention, that the elemental chemical analysis data of the TZD complexes have a small differences falling within experimental errors.

Thermogravimetric analyses. Thermogravimetric analysis was carried out in order to confirm the composition and structures of the synthetic charge transfer complexes. The measurements were performed under static nitrogen environments within temperature range of 30–600°C (Fig. 4). The TG thermograms of the TZD–PA, TZD–DDQ, TZD–TCNQ, TZD–DCQ, TZD–DBQ, and TZD–NBS complexes indicate that they were thermally decomposed

Table 2. Kinetic parameters determined using the Coats–Redfern (CR) and Horowitz–Metzger (HM) methods

Complex	Method	Parameter					r
		E, kJ/mol	A, s^{-1}	ΔS, J mol^{-1} K^{-1}	ΔH, kJ/mol	ΔG, kJ/mol	
PA (**I**)	CR	87	2.15E+06	–126	85	152	0.9874
	HM	101	2.50E+08	–87	98	144	0.9753
DDQ (**II**)	CR	90	3.95E+05	–140	85	170	0.9918
	HM	100	8.85E+06	–115	95	166	0.9977
TCNQ (**III**)	CR	52	9.12E+01	–210	47	169	0.9941
	HM	61	1.82E+03	–185	56	164	0.9910
DCQ (**IV**)	CR	65	7.32E+02	–190	60	193	0.9987
	HM	85	1.92E+04	–172	76	195	0.9954
DBQ (**V**)	CR	82	1.09E+04	–169	75	187	0.9966
	HM	99	7.54E+05	–143	93	183	0.9933
NBS (**VI**)	CR	59	1.01E+02	–211	54	199	0.9932
	HM	72	1.09E+03	–195	64	198	0.9940

in two-to-five degradation steps. The maximum differential thermal analysis DTG_{max} of the first decomposition steps located within the temperature range of 44–367°C, which have a weight losses of approximately 49.23, 2.78, 12.74, 74.04, 3.18, and 43.66%, for the PA, DDQ, TCNQ, DCQ, DBQ and NBS complexes, respectively. These results are attributed to the complete or partial loss of the acceptor moiety. The total mass losses of the six TZD charge transfer complexes are 84.17, 84.33, 56.80, 95.05, 77.75, and 96.31% for the PA, DDQ, TCNQ, DCQ, DBQ and NBS complexes, respectively.

Thermodynamic data. Two different common methods were employed to evaluate the kinetic thermodynamic parameters: the Coats–Redfern method [37] and the Horowitz–Metzger method [38]. The thermodynamic parameters (i.e., the activation energy (E^*), the frequency factor (A), the enthalpy of activation (H^*), the entropy of activation (S^*) and the Gibbs free energy of activation (G^*) associated with the TZD complexes were evaluated graphically and the obtained data are listed in Table 2. The kinetic data obtained from the two methods are comparable and can be considered in good agreement with each other. The activation energy (E^*) of the complexes is expected to increase with the increasing thermal stability of complexes. Therefore, the E^* value for the DDQ complex is higher compared to the other complexes, which indicates the higher thermal stability of the TZD-DDQ complex. By comparing the E^* values for the main decomposition stage of the TZD complexes, we observed the following trend for the different acceptors: DDQ > PA > DBQ > DCQ > NBS > TCNQ. These differences may be due to the reactivity of the complexes and the electronic configuration of the acceptor when complexing with the TZD donor. The entropy of activation (ΔS^*) is found to be negative in all cases, which indicates that the decomposition reactions proceed spontaneously and the activation complexes have more ordered structure than the reactants. The ΔS^* values of the TZD charge transfer complexes occur in a increasing order as follows: TZD–PA > TZD–DDQ > TZD–DBQ > TZD–DCQ > TZD–TCNQ > TZD–NBS. The satisfactory values for the correlation coefficients from the Arrhenius plots of the thermal decomposition steps were observed to be ~ 1 for all cases, which indicates a good fit with the linear function and reasonable agreement between the experimental data and the kinetic parameters.

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