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### Journal of Molecular Structure



# Charge-transfer complexes of sulfamethoxazole drug with different classes of acceptors

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#### ARTICLE INFO

Article history: Received 20 May 2010 Received in revised form 1 July 2010 Accepted 1 July 2010 Available online 8 July 2010

Keywords: Sulfamethoxazole Charge-transfer complexes TG/DTG IR Acceptor

#### ABSTRACT

The charge-transfer complexes of the donor sulfamethoxazole (SZ) with iodine (I<sub>2</sub>), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), *p*-chloranil (CHL) and picric acid (PA) have been studied spectrophotometrically in chloroform or methanol at room temperature using absorption spectrophotometer. The results indicate that formation of CT-complexes in case of four acceptors. The stoichiometry of the complexes was found to be 1:1 ratio by molar ratio method between donor and acceptor with maximum absorption bands (CT band). The data are discussed in terms of formation constant ( $K_{CT}$ ), molar extinction coefficient ( $\varepsilon_{CT}$ ), standard free energy ( $\Delta G^{\circ}$ ), oscillator strength (f), transition dipole moment ( $\mu$ ), resonance energy ( $R_N$ ) and ionization potential ( $I_D$ ). The results indicate that the formation constant ( $K_{CT}$ ) for the complexes were shown to be dependent upon the nature of electron acceptor, donor and polarity of solvents which were used. IR, <sup>1</sup>H NMR, mass spectra, UV–Vis techniques, elemental analyses (CHN) and TG–DTG investigation were used to characterize the four sulfamethoxazole charge-transfer complexes.

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#### 1. Introduction

Sulfamethoxazole (Formula 1) is a sulfonamide bacteriostatic antibiotic. It is most often used as part of a synergistic combination with trimethoprim in a 5:1 ratio in co-trimoxazole, also known under trade names such as Bactrim, Septrin, or Septra. Its primary activity is against susceptible forms of Streptococcus, *Staphylococcus aureus, Escherichia coli, Haemophilus influenzae*, and oral anaerobes. It is commonly used to treat urinary tract infections. In addition it can be used as an alternative to amoxicillin-based antibiotics to treat sinusitis. It can also be used to treat toxoplasmosis.

The charge-transfer interactions between sulfamethoxazole electron donor and electron acceptors are generally associated with the formation of intensely colored charge-transfer complexes, which absorb radiation in the visible region. A variety of electron donating compounds have been reported to yield charge-transfer complexes leads to their utility in the development of simple and convenient colorimetric methods [1–4].

Charge-transfer complexes are known to take part in many chemical reactions like addition, substitution and condensation [5,6]. These complexes have great attention for non-linear optical materials and electrical conductivities [7–10]. Electron donor–

acceptor CT-interaction is also important in the field of drugreceptor binding mechanism [11], in solar energy storage [12] and in surface chemistry [13] as well as in many biological fields [14]. On the other hand, the CT-reactions of certain  $\pi$ -acceptors have successfully utilized in pharmaceutical analysis [15]. For these wide applications extensive studies on CT-complexes of  $\pi$ -acceptors have been performed [16].

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 [17,18]. Also, protonation of the donor from acidic acceptors are generally rout for the formation of ion pair adducts [19–21].

The solid charge-transfer complexes formed between iodine and several types of electron donors such as aromatic hydrocarbons, polycyclic amine, mixed oxygen/nitrogen cyclic bases, aromatic/aliphatic amines have been studied and categorized [22–30]. Some of charge-transfer complexes show very interesting applications in the analysis of some drugs in pure form or in pharmaceutical preparations [31,32].

The charge-transfer reactions of (SZ) with  $(I_2)$ , (DDQ), (CHL) and (PA) have not yet been reported in the literature; therefore the aim of the present study was directed to investigate these reactions.

Results of elemental analysis for all the sulfamethoxazole charge-transfer complexes are listed in Table 1. From the table, it can seen that values found are in agreement with the calculated ones, and the composition of the CT-complexes is matched with





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<sup>0022-2860/\$ -</sup> see front matter @ 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2010.07.004



Formula 1. Sulfamethoxazole (SZ).

the molar ratios presented from the photometric titration occurs between (SZ) and acceptors ( $\sigma$ - and  $\pi$ -acceptor). All the complexes are insoluble in cold and hot water, but easily soluble in DMF and DMSO.

#### 2. Experimental

2.1. Preparation of sulfamethoxazole/acceptor charge-transfer complexes (acceptor =  $I_2$ , DDQ, CHL and PA)

Sulfamethoxazole (SZ) ( $C_{10}H_{11}N_3O_3S$ ) was of analytical reagent grade (Merck reagent). The different  $\sigma$ - and  $\pi$ -acceptors were purchased from Aldrich. Stock solutions of sulfamethoxazole and acceptors were freshly prepared and the spectroscopic grade chloroform (Merck Co.) and methanol (BDH) were used as received.

#### 2.1.1. [Sulfamethoxazole]-iodine CT-complex

The solid CT-complex of SZ with iodine was prepared by mixing 1.0 mmol of the SZ donor in 20 ml chloroform, a solution of iodine was added (253.81 mg, 1.0 mmol) in the same solvent with continuously stirring for about 15 min at room temperature. A dark brown precipitate solution was appearing and allowed to evaporate slowly at room temperature. A dark brown precipitate complex was formed, washed several times with little amounts of chloroform, and dried under vacuum over anhydrous calcium chloride; the empirical formula of the complex  $[(SZ)_2]I^+ \cdot I_3^-$  is  $C_{20}H_{22}N_6O_6S_2I_4$  with molecular weight 1014.22 g/mol.

#### 2.1.2. [Sulfamethoxazole]/DDQ, CHL and PA CT-complexes

The solid CT-complexes of SZ with  $\pi$ -acceptors like (DDQ, CHL and PA) were prepared by mixing 1 mmol of the SZ donor in 10 ml chloroform with 1 mmol of each acceptor in the same solvent with constant stirring for about 15 min. The solutions were allowed to evaporate slowly at room temperature, the resulted complexes in the solid state filtered and washed several times with little amounts of solvent and dried under vacuum over anhydrous calcium chloride. The charge-transfer complexes [(SZ)(DDQ)] (dark green powder) formed with empirical formula C<sub>18</sub>H<sub>11</sub>N<sub>5</sub>SCl<sub>2</sub>O<sub>5</sub> with molecular weight 480.31 g/mol, [(SZ)(CHL)] (red crystals) formed with empirical formula as C<sub>16</sub>H<sub>11</sub>N<sub>3</sub>SCl<sub>4</sub>O<sub>5</sub> with molecular weight 499.18 g/mol and [(SZ)(PA)] (yellow crystals) formed with empirical formula C<sub>16</sub>H<sub>14</sub>N<sub>6</sub>SO<sub>10</sub> with molecular weight 482.41 g/ mol.

#### 2.2. Instrumentation and physical measurements

#### 2.2.1. Electronic spectra

The electronic spectra of the donors, acceptors and the resulted CT-complexes were recorded in the region of (200–800 nm) by using a Jenway 6405 Spectrophotometer with quartz cells, 1.0 cm path in length.

#### 2.2.2. Infrared spectra

IR measurements (KBr discs) of the solid donors, acceptor and CT-complexes were carried out on a Bruker FT-IR spectrophotometer  $(400-4000 \text{ cm}^{-1})$ .

#### 2.2.3. <sup>1</sup>H NMR spectra

<sup>1</sup>H NMR spectra were obtained on a Varian Gemini 200 MHz spectrometer. <sup>1</sup>H NMR data are expressed in parts per million (ppm), referenced internally to the residual proton impurity in DMSO (dimethylsulfoxide,  $d_6$ ) solvent and the reported of chemical shift (m = multiplet, s = singlet and br = broad).

#### 2.2.4. Mass spectra

The compositions of the complexes were confirmed from mass spectra at 70 eV by using AEI MS 30 mass spectrometer.

#### 2.2.5. Thermal analysis

The thermal analysis (TGA/DTG) was carried under nitrogen atmosphere with a heating rate of 10 C/min using a Shimadzu TGA-50H thermal analyzers.

#### 3. Results and discussion

## 3.1. Electronic absorption spectrum of SZ/iodine, SZ/DDQ, SZ/CHL and SZ/PA systems

The electronic UV–Vis absorption spectrum of the iodine, DDQ, CHL and PA complexes were measured in CHCl<sub>3</sub> or MeOH solvents. In case of CHCl<sub>3</sub> or MeOH solvents the complexes are formed by adding X ml of  $5.0 \times 10^{-4}$  M (iodine, DDQ, CHL or PA) (X = 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50 and 3.00 ml) to 1.00 ml of  $5.0\times 10^{-4}\,M$  sulfamethoxazole. The volume of the mixtures in each case was completed to 10 ml with the respected solvent. The concentration of SZ in the reaction mixture was kept fixed at  $0.50\times 10^{-4}\,\text{M}$  in the  $\text{CHCl}_3$  or MeOH solvents, while, the concentration of the solvents of the sol tration of iodine, DDQ, CHL or PA was varied over the range of  $0.125\times 10^{-4}\,M$  to  $1.500\times 10^{-4}\,M$  for SZ/I2, SZ/DDQ, SZ/CHL or SZ/PA systems in  $\mbox{CHCl}_3$  or MeOH solvents. These concentrations produce SZ:acceptor (I2, DDQ, CHL and PA) ratios extending along the range from 1:0.25 to 1:3.00. The electronic absorption spectra of the 1:1 ratios in  $CHCl_3$  or MeOH together with the reactants ( $I_2$ , DDO, CHL, PA and SZ are shown in Figs. 1A-1D.

The spectra show characteristic real absorption bands which are not present in the spectra of the reactants free iodine, DDQ, CHL, PA and SZ. These bands are assigned at (362 and 285 nm), (540 and 410 nm), 310 nm and 380 nm due to the CT-complexes formed in the reaction of SZ with  $I_2$ , DDQ, CHL and PA, respectively, in the

Table 1

Elemental analysis CHN and physical parameters data of the CT-complexes formed in the reaction of the SZ with iodine, DDQ, CHL and PA.

Complexes	Mwt	С%		H%	Н%		N%		Physical data	
		Found	Calc.	Found	Calc.	Found	Calc.	$\Lambda_{\rm m}(\mu s)$	Mp (°C)	
$[(SZ)_2]I^+ \cdot I_3^-$	1014	23.55	23.67	2.13	2.17	8.14	8.28	45	56	
[(SZ)(DDQ)]	481	44.56	44.91	2.25	2.29	14.26	14.55	21	104	
[(SZ)(CHL)]	499	38.32	38.48	2.16	2.20	8.33	8.42	18	112	
[SZ)(PA)]	482	39.77	39.83	2.84	2.90	17.28	17.43	36	124	



**Fig. 1A.** Electronic absorption spectra of; SZ–iodine reaction in CHCl<sub>3</sub>, where (*d*) = donor  $(1.0 \times 10^{-4} \text{ M})$ , (*a*) = acceptor  $(1.0 \times 10^{-4} \text{ M})$  and (*c*) = CT-complex.



**Fig. 1B.** Electronic absorption spectra of; SZ–DDQ reaction in MeOH, where (*d*) = donor  $(1.0 \times 10^{-4} \text{ M})$ , (*a*) = acceptor  $(1.0 \times 10^{-4} \text{ M})$  and (*c*) = CT-complex.



**Fig. 1C.** Electronic absorption spectra of; SZ–CHL reaction in MeOH, where (*d*) = donor  $(1.0 \times 10^{-4} \text{ M})$ , (*a*) = acceptor  $(1.0 \times 10^{-4} \text{ M})$  and (*c*) = CT-complex.

chloroform for iodine system and in methanol solvent in case of DDQ, CHL and PA. Table S1(A–D) gives the values of the absorbance's obtained from photometric titrations based on the distin-



**Fig. 1D.** Electronic absorption spectra of; SZ–PA reaction in MeOH, where (*d*) = donor  $(1.0 \times 10^{-4} \text{ M})$ , (*a*) = acceptor  $(1.0 \times 10^{-4} \text{ M})$  and (*c*) = CT-complex.



Fig. 2A. Photometric titration curve for the  $\text{SZ-I}_2$  system in  $\text{CHCl}_3$  at 285 and 362 nm.



Fig. 2B. Photometric titration curve for the SZ-DDQ system in MeOH at 540 nm.

guished absorption bands around (362 and 285 nm), (540 and 410 nm), 310 nm and 380 nm. Photometric titration curves based on these characterized absorption bands are given in Figs. 2A–2D.



Fig. 2C. Photometric titration curve for the SZ-CHL system in MeOH at 310 nm.



Fig. 2D. Photometric titration curve for the SZ-PA system in MeOH at 380 nm.



**Fig. 3A.** The plot of  $(C_d^o + C_a^o)$  values against  $(C_d^o \cdot C_a^o/A)$  values for the SZ-iodine system in CHCl<sub>3</sub> at 362 and 285 nm.

These photometric titration curves were obtained according to the known methods [33] by the plot of the absorbance against the X ml added of the iodine  $\sigma$ -acceptor or (DDQ, CHL and PA) as  $\pi$ -acceptors. The equivalence points shown in these curves clearly



**Fig. 3B.** The plot of  $(C_d^o + C_a^o)$  values against  $(C_d^o \cdot C_a^o/A)$  values for the SZ–DDQ system in MeOH at 540 nm.



**Fig. 3C.** The plot of  $(C_d^o + C_a^o)$  values against  $(C_d^o \cdot C_a^o/A)$  values for the SZ–CHL system in MeOH at 310 nm.

indicate that the formed CT-complexes between SZ and (iodine, DDQ, CHL or PA) are 1:1. The formation of 1:1 complex was strongly supported by elemental analysis, mass spectra as well as thermal analysis TG-DTG.

However, the appearance of the two absorption bands around  $\approx$ 360 and  $\approx$ 290 nm are well known [34–36], to be characteristic for the formation of the tri-iodide ion ( $I_3^-$ ). Accordingly, the formed complex was formulated as [(SZ)<sub>2</sub>]I<sup>+</sup> · I<sub>3</sub><sup>-</sup>.

It was of interest to observe that the solvent has a pronounced effect on the spectral intensities of the formed  $[(SZ)_2]I^+ \cdot I_3^-$ , [(SZ)(DDQ)], [(SZ)(CHL)] and [(SZ)(PA)] complexes. The 1:1 modified Benesi–Hildebrand equation [37] was used in the calculations.

$$\frac{C_a^o C_d^o l}{A} = \frac{1}{K\varepsilon} + \frac{C_a^o + C_d^o}{\varepsilon}.$$
(1)

where  $C_a^o$  and  $C_d^o$  are the initial concentrations of the acceptors (I<sub>2</sub>, DDQ, CHL or PA) and the donor SZ, respectively, and *A* is the absorbance of the definite bands around (362 and 285 nm), (540 and 410 nm), 310 nm and 380 nm. The data obtained  $C_d^o$  of SZ,  $C_a^o$  of (I<sub>2</sub>, DDQ, CHL or PA),  $(C_a^o+C_d^o)$  and  $(C_a^o\cdot C_d^o/A)$  in CHCl<sub>3</sub> or MeOH solvents are summarized and given in Table S2(A–D). When the  $C_a^o \cdot C_d^o/A$  values for each solvent are plotted against the corresponding  $(C_a^o + C_d^o)$  values. Straight lines are obtained with a slope of  $1/\varepsilon$ 



**Fig. 3D.** The plot of  $(C_d^o + C_a^o)$  values against  $(C_d^o \cdot C_a^o/A)$  values for the SZ–PA system in MeOH at 380 nm.

and intercept of  $1/k\varepsilon$  as shown in Figs. 3A–3D for the reaction in CHCl<sub>3</sub> or MeOH. The oscillator strength *f* was obtained from the approximate formula [38]:

$$f = (4.319 \times 10^{-9}) \varepsilon_{\max} \cdot v_{1/2}$$
(2)

where  $v_{1/2}$  is the band-width for half-intensity in cm<sup>-1</sup>. The oscillator strength values together with the corresponding dielectric constants, *D*, of the solvent used are given in Table 2. The trend of the values in this table reveals several facts. (i) The  $[(SZ)_2]I^+ \cdot I_3^-$ , [(SZ)(DDQ)], [(SZ)(CHL)] and [(SZ)(PA)] shows high values of both the equilibrium constant (*K*) and extinction coefficient ( $\varepsilon$ ). This high value of (*K*) reflects the high stability of the SZ complexes as a result of the expected high donation of the SZ, while the high value of ( $\varepsilon$ ) concerning SZ/iodine CT-complex agrees quite well with the existence of tri-iodide ion,  $I_3^-$ , which is known to have high absorptivity value [34–36]. (ii) The 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 [30].

The general mechanism for the formation of  $[(SZ)_2]I^+\cdot I_3^-$  complex is proposed as follows,

$$\begin{split} &2SZ+I_2\rightarrow [SZ]_2I^+\cdot I^-\\ &[SZ]_2I^+I^-+I_2\rightarrow [(SZ)_2]I^+\cdot I_3^- \end{split}$$

The formation of  $[SZ]_2I^+.I^-$  reaction intermediate is analogous to the well known species  $[(donor)I]^+.I^-$  formed in the reaction of iodine with many donors [39,40].

The transition dipole moment ( $\mu$ ) of the SZ CT-complexes, Table 2, have been calculated from the following Eq. (3) [41]:

$$\mu = 0.0958 [\varepsilon_{\text{max}} \cdot v_{1/2} / v_{\text{max}}]^{1/2}$$
(3)

The ionization potential  $(I_p)$  of the free (SZ) donor was determined from the CT energies of the CT band of its complexes with (iodine) by using the following relationships [42]:

$$E_{\rm CT} = I_{\rm p} - 5.2 + 1.5/(I_{\rm p} - 5.2) \tag{4a}$$

The ionization potentials of the donor  $(I_D)$  in the charge-transfer complexes of (SZ/DDQ, SZ/CHL or SZ/PA) are calculated using empirical equation derived by Aloisi and Piganatro [43].

$$I_{\rm D} \ (\rm eV) = 5.76 + 1.53 \times 10^{-4} v_{\rm CT} \tag{4b}$$

where  $E_{\text{CT}}$  is the energy of the charge-transfer of the SZ complexes, the energy of the  $\pi$ - $\sigma^*$ , n- $\sigma^*$ , n- $\pi^*$  or n- $\pi^*$  interaction ( $E_{\text{CT}}$ ) is calculated using the following equation [41]:

$$E_{\rm CT} = (hv_{\rm CT}) = 1243.667 / \lambda_{\rm CT} \ (nm) \tag{5}$$

where  $\lambda_{CT}$  is the wavelength of the complexation band.

Determination of resonance energy  $(R_N)$ , from Briegleb and Czekalla [44] theoretically derived the relation;

$$\varepsilon_{\rm max} = 7.7 \times 10^{-4} / [h v_{\rm CT} / [R_{\rm N}] - 3.5] \tag{6}$$

where  $\varepsilon_{\text{max}}$  is the molar extinction coefficient of the complex at the maximum of the CT absorption,  $v_{\text{CT}}$  is the frequency of the CT peak and  $R_{\text{N}}$  is the resonance energy of the complex in the ground state, which, obviously is a contributing factor to the stability constant of the complex (a ground state property). The values of  $R_{\text{N}}$  for the (iodine, DDQ, CHL and PA) complexes under study have been given in Table 2. The standard free energy changes of complexation ( $\Delta G^{\circ}$ ) were calculated from the association constants by the following equation derived by Martin et al. [45].

$$\Delta G^{\circ} = -2.303 RT \log K_{\rm CT} \tag{7}$$

where  $\Delta G^{\circ}$  is the free energy change of the complexes (kJ mol<sup>-1</sup>), *R* is the gas constant (8.314 J mol<sup>-1</sup> K), *T* is the temperature in Kelvin degrees (273 + °C) and  $K_{CT}$  is the association constant of the complexes (l mol<sup>-1</sup>) in different solvents at room temperature. The values thus calculated are represented in Table 2.

# 3.2. Infrared spectra of the SZ/iodine, SZ/DDQ, SZ/CHL and SZ/PA solid complexes

The mid infrared spectra of SZ and the formed CT-complex,  $[(SZ)_2]I^+ \cdot I_3^-$ , were recorded from KBr discs. These spectra are shown in Fig. S1(A and B), respectively. The spectral bands are assigned into their vibrational modes and given in Table 3. As expected, the bands characteristic for the SZ unit in  $[(SZ)_2]I^+ \cdot I_3^-$  CT-complex are shown with small changes in band intensities and frequency values. For example, the v(N-H) vibrations of  $-NH_2$  occur at 3468 and 3378 cm<sup>-1</sup> for free SZ due to  $v_{as}(NH)$  and  $v_s(NH)$ , respectively. The hypochromic effect (decreasing in the intensity of v(NH) vibrations in case of iodine complex rather than SZ alone as

Table 2

Spectrophotometric results of the SZ CT-complex with iodine, DDQ, CHL and PA in CHCl<sub>3</sub> or MeOH solvents at 25 °C.

$\lambda_{\max}$ (nm)	$E_{\rm CT}~({\rm eV})$	K (l mol <sup>-1</sup> )	$\varepsilon_{\rm max} ({\rm l}{\rm mol}^{-1}{\rm cm}^{-1})$	$f  imes 10^3$	$\mu  imes 10^3$	Ip	D	R <sub>N</sub>	$\Delta G^{\circ}$ (25 °C) kJ mol <sup>-1</sup>
$[(SZ)_2]I^+ \cdot I_3^-$ 362	3.43	$\textbf{7.45}\times 10^4$	$221\times 10^4$	0.018	0.372	9.99	4.70	0.980	27.80
[(SZ)(DDQ)] 410	3.03	$\textbf{2.26}\times 10^4$	$\textbf{73.6}\times 10^4$	0.448	0.227	8.59	33	0.866	24.80
[(SZ)(CHL)] 310	4.01	$16.9\times10^4$	$15.3\times10^4$	0.179	0.108	10.70	33	1.150	29.80
[(SZ)(PA)] 380	3.27	$\textbf{2.34}\times 10^4$	$443\times 10^4$	35.5	0.536	9.79	33	0.934	24.90

#### Table 3

Infrared frequencies  $^a$   $(cm^{-1})$  and tentative assignments for SZ donor and  $[(SZ)_2]l^+ \cdot l_3^-$  complex.

SZ	$[(SZ)_2]I^+\cdot I_3^-$	Assignments <sup>b</sup>
3468 s	3470 mw	$v(N-H)$ ; $-NH_2$ and $-NH$
3378 vs	3385 mw	v(C–H); aromatic
3299 vs	3208 w	
3143 s	3144 vw	
2929 w	2983 w	$v_{s}(C-H) + v_{as}(C-H); CH_{3}$
2858 w	2853 w	
-	-	Hydrogen bonding
1622 vs	1619 vs	v(C=C)
1596 vs	1597 sh	$\delta_{def}(N-H)$
		Ring breathing bands
1503 s	1500 ms	C-H deformation
1471 s	1466 ms	
	1400 w	
1365 s	1372 mw	v(C-C)
1309 s	1311 s	v(C-N)
1266 ms	1264 mw	v(C-O)
1148 vs	1156 vs	$v(SO_2)$
1091 ms	1091 ms	
1025 mw	1033 ms	
927 ms	929 ms	(C–H) bend
884 ms	881 ms	$\delta_{rock}$ ; NH
	830 ms	
	786 w	
684 vs	753 vw	CH <sub>2</sub> rock
644 w	681 ms	Skeletal vibrations
577 w	568 s	CNC deformation
547 vs		

<sup>a</sup> s = Strong, w = weak, m = medium, sh = shoulder, v = very, br = broad. <sup>b</sup> v, Stretching;  $\delta$ , bending.

### I—I—I Formula 2.

well as the blue shifted in the wavenumbers from  $3299 \text{ cm}^{-1}(\text{SZ})$  to  $3208 \text{ cm}^{-1}(\text{iodine complex})$ . Such these changes clearly indicate that the lone pair of electron of NH<sub>2</sub> in sulfamethoxazole donor is participated in the complexation process with iodine. On the other hand, the absence of a few bands at around  $2600-2400 \text{ cm}^{-1}$  (hydrogen bonding) in the SZ/iodine complex [46], strongly interpretive the mode of interaction between SZ and iodine through lone pair of electron of NH<sub>2</sub> not *via* forming hydrogen bond between –NH group in SZ donor and iodine acceptor (N–H–I).

#### 3.2.1. Group theoretical analysis of $I_3^-$

The geometry of  $I_3^-$  in  $[(SZ)_2]I^+ \cdot I_3^-$  may belong to one of the two structures; linear structure with  $(D_{\infty h})$  symmetry and non-linear structure with  $(C_{2\nu})$  symmetry. The linear  $I_3^-$  ion is shown in Formula 2. It possesses an infinite rotation axis  $C_{\infty}$ , an infinite number of  $C_2$  axes, an infinite inversion axis  $S_{\infty}$ , an infinite number of vertical planes  $\infty \sigma_{\nu}$ , a horizontal plane of symmetry  $\sigma_h$ , and a center of symmetry. The  $C_2$  axes are perpendicular to  $C_{\infty}$ , and thus it belongs to  $D_{\infty h}$  symmetry.

The number of vibrations,  $\Gamma_{\text{vib}}$  belongs to each type of symmetry may evaluated according to the formula [47]:

$$\Gamma_{\rm vib} = 1/g \sum n_{\rm R} \cdot X_{\rm (R)} \cdot X_{\rm p}({\rm R})$$

where *g* is the number of all symmetry operation (symmetry elements) and  $n_{\rm R}$  – is the number of symmetry operation of the same type, while  $X_{\rm (R)}$  is the character of a given operation in any representation as illustrated in the D<sub>∞h</sub> – character table, Table S3, and X<sub>p</sub>(R) is the multiplication of the number of unshifted atoms per each symmetry operation, Table S4, and the contribution per each symmetry operation in  $\Gamma_{3N}$  Table S5.

$$I \xrightarrow{\longleftarrow} I \xrightarrow{\longrightarrow} I$$

$$v_{s}(I \longrightarrow I); \Sigma_{g}^{+}$$

$$I \xrightarrow{\longrightarrow} I \xrightarrow{\longrightarrow} I$$

$$v_{as}(I \longrightarrow I); \Sigma_{u}^{+}$$

$$V_{as}(I \xrightarrow{} I); \pi_{u}$$









**B<sub>2</sub>-Motion:** 

**2A<sub>1</sub>-Motions:** 

$$I = I$$

$$v_{as}(I = I); B_2$$

$$(147 \text{ cm}^{-1})$$

Formula 5. Vibration of non-linear I3 ion.

Accordingly, the numbers of vibrations ( $\Gamma_{vib}$ ) for the linear  $l_3^-$  ion with  $D_{\infty h}$  symmetry are distributed as follows;

$$\Gamma_{\text{vib}} = \sum_{g}^{+}(\mathbf{R}) + \sum_{u}^{-} \mathbf{IR} + \pi_{u}(\mathbf{IR})$$

where R and IR refer to their Raman and infrared activities, respectively. Formula 3 describes the nature of these vibrational motions of  $I_3^-$  ion under the  $D_{\infty h}$  symmetry.

The non-linear triiodide  $I_3^-$  ion Formula 4 has two fold axis of symmetry,  $C_{2v}$ , and two  $\sigma_v$  planes of symmetry, thus it belongs to  $C_n$ , symmetry. The number of vibrations,  $\Gamma_{vib}$ , belongs to each type of symmetry may evaluate according to the formula:

$$\Gamma_{\mathrm{vib}} = 1/g \sum n_{\mathrm{R}} \cdot \mathrm{X}_{(\mathrm{R})} \cdot \mathrm{X}_{\mathrm{p}}(\mathrm{R})$$

Their values for  $C_{2v}$  are represented in Tables S6–S8, respectively.

Accordingly, the numbers of vibrations ( $\Gamma_{vib}$ ) for non-linear  $I_3^-$  ion with  $C_{2v}$  symmetry are distributed as follows:

$$\Gamma_{vib} = 2A_1(IR \text{ and } R) + B_2(IR \text{ and } R)$$

where IR and R represent their infrared and Raman activities, respectively. Formula 5 describes the nature of these vibrational motions of non-linear  $I_3^-$  ion with  $C_{2v}$  symmetry.

#### Table 4

Infrared frequencies<sup>a</sup> (cm<sup>-1</sup>) and tentative assignments for DDQ, CHL, PA, [(SZ)(DDQ)], [(SZ)(CHL)] and [(SZ)(PA)] CT-complexes.

DDQ	CHL PA		[(SZ)(acceptor)]	CT-complexes	Assignments <sup>b</sup>	
			DDQ	CHL	PA	
3325 w 3218 br	3354 ms	3416 br 3103 ms	3460 mw 3374 ms 3221 vw 3161 vw 3072 vw	3467 ms 3378 ms 3295 w 3243 w 3143 w	3341 s,br 3178 s,br 3095 s	$v_{(0-H)}$ v(N-H); -NH <sub>2</sub> and -NH v(C-H); aromatic $v(^*NH_3)$
-	-	2980 sh 2872 w	2984 vw 2880 vw	2927 vw 2853 vw	2845 br	$v_{s(C-H)} + v_{as(C-H)}$
-	-	-	2784 w 2650 vw	-	– 2599 br	Hydrogen bonding v(*NH <sub>3</sub> )
2250 vw 2231 ms	-	-	2252 w	-	-	$v_{(C=N)}$ ; DDQ
1673 vs	1685 vs	1861 ms 1632 vs 1608 vs 1529 vs	1692 s 1619 s 1592 s	1685 vs 1619 s	1612 vs	$v(NO_2)$ ; PA $v_{(C=0)} + v_{(C=N)}$ $\delta(^*NH_3)$
-	-	-	1557 ms	1571 s	1571 w	$\delta_{ m def}( m N- m H)$ Ring breathing bands
1552 vs 1451 s	1567 vs 1487 w	1432 s	1459 s	1503 s 1472 s	1537 s 1466 s 1430 s	$v_{(C=C)}$ C-H deformation
1358 w 1267 s 1172 vs 1072 w	1316 w 1257 s 1232 s 1210 vw 1110 vs	1343 ms 1312 w 1263 w 1150 ms 1086 s	1398 ms 1320 ms 1265 ms 1159 vs 1089 ms 1036 w	1366 s 1310 s 1259 s 1160 s 1110 vs 1030 w	1393 s 1321 vs 1281 sh 1171 vs 1086 s	$v_{(C-C)} + v_{(C-N)}$ $v(C-O) + v(SO_2)$ CH, in-plane bend
1010 vw 893 s 800 vs 720 s	903 s 750 s 709 s	917 vs 829 w 781 s 732 s	1007 vw 938 w 890 w 833 mw 794 s 745 mw	927 w 888 w 831 w 751 s 711 ms	1011 s 929 s 834 s 786 s 714 s	$\delta_{\text{TOCK}}$ ; NH CH-deformation $v_{(C-CI)}$
615 ms 527 vw	-	703 s 652 sh	674 ms	683 s	665 s	Skeletal vibration CH bend
457 ms 432 mw	471 mw	522 ms	575 ms 545 ms	574 s 548 s	575 s 549 s 500 vw	CH out of plane bend Skeletal vibration CNC def. &(ONO); PA

 $^a~s$  = Strong, w = weak, m = medium, sh = shoulder, v = very, br = broad.  $^b~v,$  Stretching;  $\delta,$  bending.



Formula 6. Structure of the [(SZ)(DDQ)] CT-complex.

From the above going discussion the shape of the  $I_3^-$  ion is nonlinear and belongs to  $C_{2v}$  symmetry. The three modes of vibrations distributed over the symmetry species  $2A_1 + B_2$  should be all infra-



Formula 7. Structure of the [(SZ)(CHL)] CT-complex.

red active. If the complex is linear, i.e. belongs to  $D_{\infty h}$  it gives only two infrared bands which is not the case.



Formula 8. Structure of the [(SZ)(PA)] CT-complex.



Fig. 4A. <sup>1</sup>H NMR spectrum of sulfamethoxazole (SZ).

The Infrared spectra of the 1:1 CT-complexes formed from the interaction of the Sulfamethoxazole (SZ) donor and the respected acceptors with the general formula,  $[(SZ)(\pi$ -acceptor)], together with the corresponding free acceptor (DDQ, CHL and PA) and donor SZ, are shown in Fig. S1. Full assignments concerning the all of infrared bands were located in the spectra are listed in Table 4.

A comparison of the relevant IR spectral bands of the free donor, SZ and acceptors (DDQ, CHL and PA) with the corresponding appeared in the IR spectra of the isolated solid CT-complexes clearly indicated that the characteristic bands of SZ show some shift in the frequencies (Table 4), as well as some change in their bands intensities. This could be attributed to the expected symmetry and electronic structure changes upon the formation of the CT-complex. The infrared explanation will take separately for each CT-complex to give an idea about the position of complexation as follows;

In the IR spectrum of the molecular complex of DDO with SZ. the  $v(C \equiv N)$  band of the free acceptor are weakness and decreased upon CT-complexation. Since DDQ is deprived from any acidic centers, thus it may be conclude that the molecular complex is formed through  $\pi - \pi^*$  and/or  $n - \pi^*$  charge migration from HOMO of the donor to the LUMO of the acceptor [48]. The interpretation of IR spectra strongly supported that the CT-interaction in case of SZ/DDQ complex occurs through  $n-\pi^*$  transition. This assumption back to the distorted and loss of the sharp bands in the -NH<sub>2</sub> region 3470–3100 cm<sup>-1</sup>, another supposition, the deprotonation of –NH<sub>2</sub> group of SZ to only one of CN groups by forming intermolecular hydrogen bonding (Formula 6). In addition, the characteristic bands of the hydrogen bond are existed in the IR spectrum of the SZ/DDQ complex at 2600-2800 cm<sup>-1</sup> with medium weak-to-weak intensities. The infrared spectrum was confirmed the 1:1 molar ratio between SZ:DDQ by the presence of one band at 2259 cm<sup>-1</sup> from two bands of 2CN groups which assigned at 2250 and 2231 for free DDQ acceptor.

In case of the infrared spectrum of [(SZ)(CHL)] CT-complex, the spectrum of the CT-complex did not exhibit any new bands indicating that no chemical reaction occurred, other than electron transfer  $(\pi - \pi^*)$  from the SZ to CHL (Formula 7). This suggestion is supported by the change in the intensities of the characteristic bands of aromatic rings (Table 4).



Fig. 4B. <sup>1</sup>H NMR spectrum of [(SZ)(PA)] charge-transfer complex.

Table 5
<sup>1</sup> H NMR data of SZ and SZ/PA compounds.

Compounds	3H; CH₃ SZ	2H; NH <sub>2</sub> SZ	1H; aromatic five member ring SZ	4H aromatic six member ring SZ	2H aromatic PA	1H; –NH
SZ	2.290	6.100	6.107	7.488, 6.598	-	10.95
[(SZ) (PA)]	2.286	6.447	6.093	7.544–6.680	8.624	10.987



Fig. 5A. Mass spectrum of sulfamethoxazole.

The vibration frequencies of the v(N-H);  $NH_2$  group for SZ observed at 3468, 3378, 3299 and 3143 cm<sup>-1</sup> is not shifted but the intensities were affected, this meaning that amino group not sharing in the CT-complexation and the  $\pi$ - $\pi$ <sup>\*</sup> transition occurs on the six member ring. The group of bands are exhibited at 2927 and 2853 cm<sup>-1</sup> in this complex were assigned to  $v_s(C-H) + v_{as}(C-H)$ vibrations with the same position wavenumbers compared with the free SZ. The stretching vibrational of v(C=0) absorption band in the case of the free CHL is appeared at 1685 cm<sup>-1</sup> and under complexation this band is still unshifted. Doubtless, the IR spectrum strongly supported that the CT-interaction in the case of SZ/CHL complex take place through  $\pi - \pi^*$  transition. The bands associated with v(C-CI) vibration that appeared at 903 and 709 cm<sup>-1</sup> in the free CHL were shifted to lower wavenumbers and decreasing in the intensities of the characteristic peaks, these results due to the increasing in the electron density around CHL moiety.

The IR spectrum of the SZ/PA CT-complex is characterized by a broad and medium-to-weak group of bands appearing in the region 2400–2800  $\text{cm}^{-1}$ , which are not appearing in the spectra of the free SZ donor and PA acceptor. These bands are attributed to the stretching vibration of a proton attached to the donation site of the donor [49]. These results caused to the protonation of the <sup>+</sup>NH<sub>2</sub> group of the donor through one protons transfer from the acidic center on the PA acceptor via -OH group to the basic center on the donor <sup>+</sup>NH<sub>2</sub> group. On the other hand the intermolecular hydrogen bond occurs in PA acceptor from on OH group to the basic center nitrogen atom. Such assumption is strongly supported by the appearance of an absorbance bands at (3178, 3095 and  $2599 \text{ cm}^{-1}$ ) and (1612 and 1537 cm $^{-1}$ ) due to stretching and bending deformation of <sup>+</sup>NH<sub>3</sub> group, respectively. This is further supported by disappear or decrease in the stretching of OH group of PA acceptor due to intermolecular hydrogen bond forming. The shift of the IR bands of the acceptor moiety to lower wavenumbers and those of the donor moiety to higher values reflects a donor to





Fig. 6A. TG-DTG curve of sulfamethoxazole free ligand.

acceptor charge-transfer of  $\pi$ - $\pi^*$  interaction,  $D_{HOMO} \rightarrow D_{LUMO}$  transition [48].

Accordingly, the hydrogen bonding between the SZ donor and the PA acceptor can be formulated as Formula 8.



Fig. 6B. TG–DTG curve of  $[(SZ)_2]I^+ \cdot I_3^-$  charge-transfer complex.



Fig. 6C. TG-DTG curve of [(SZ)(DDQ)] charge-transfer complex.



Fig. 6D. TG–DTG curve of [(SZ)(CHL)] charge-transfer complex.

#### 3.3. <sup>1</sup>H NMR spectrum of [(SZ)(PA)] complex

<sup>1</sup>H NMR spectra of (SZ) free donor and [(SZ)(PA)] CT-complex in DMSO at room temperature were measured and given in Figs. 4A and 4B. The chemical shifts (ppm) of proton NMR for the detected peaks are assigned and listed in Table 5. Evidently, the results obtained from elemental analysis, infrared spectra, and photometric titrations met in the same point with <sup>1</sup>H NMR spectra to interpret the mode of interaction between donor and acceptor as follows:



Fig. 6E. TG-DTG curve of [(SZ)(PA)] charge-transfer complex.



**Fig. 7A.** Kinetic curves of decomposition steps of SZ compound, where (CR) Coats and Redfern (CR) integral method and (HM) Horowitz and Metzger (HM) approximation method.

- i. In the [(SZ)(PA)] CT-complex, the signal distinguish to H proton of OH acceptor at  $\sim$ 12 ppm disappeared due to deprotonation from acceptor to donor, beside that, the shift in H of NH<sub>2</sub> (SZ) from 6.10 ppm to 6.447 ppm.
- ii. The downfield (higher shift) of most signals in the SZ/PA CTcomplex due to the interaction occur between donor and acceptor.



**Fig. 7B.** Kinetic curves of decomposition steps of SZ/iodine CT-complex, where (CR) Coats and Redfern (CR) integral method and (HM) Horowitz and Metzger (HM) approximation method.

#### 3.4. Mass spectrum of [(SZ)(DDQ)] complex

Mass spectrometry has been applied in order to study the main fragmentation routes of sulfamethoxazole/DDQ charge-transfer complex. Differences in fragmentation were caused by the nature of the attached acceptors through the intermolecular hydrogen bond between SZ and DDQ, while the observed peak characterized to DDQ  $C_6H_2OH(NO_3)_3$  at m/z 227, is detected in the fragmentation of SZ/DDQ CT-complex. In Figs. 5A and 5B, the base peak existed at m/z = 92 for SZ/PA is assigned to Ar–NH<sub>2</sub>.

SZ/DDQ CT-complex also shows series of peaks at 198, 174, 156, 140, 124, 108 and 65 amu corresponding to various fragments. The intensities of these peaks give the idea of the stabilities of the fragments.

#### 3.5. Thermal analysis studies

It seemed of interest to evaluate the effect of heating on the thermal stability of the prepared SZ CT-complexes. From TG–DTG curves (Figs. 6A–6E), the SZ donor beginning decomposed at 200 °C with maximum decomposition at 259 °C. The thermal decomposition of SZ occurs completely in one step which was observed at 259 °C within the range of 25–800 °C corresponding to loss of C<sub>3</sub>H<sub>11</sub>N<sub>3</sub>SO<sub>3</sub> organic moiety representing a weight loss of (obs. = 66.60%, calc. = 66.80% then leaving residual carbon as final fragment.

Figs. 6A–6E,  $[(SZ)_2]I^+ \cdot I_3^-$  CT-complex was thermally decomposed in two successive decomposition steps within the temperature range 25–800 °C. The first decomposition step (obs. = 11.94%, calc. = 12.51%) within the temperature range 25–200 °C, may be



**Fig. 7C.** Kinetic curves of decomposition steps of SZ/DDQ CT-complex, where (CR) Coats and Redfern (CR) integral method and (HM) Horowitz and Metzger (HM) approximation method.

attributed to the liberation of  $1/2I_2$  molecule. The second decomposition step found within the temperature range 200–800 °C (obs. = 50.10%, calc. = 49.17%) which are reasonably accounted by the removal of  $H_{22}O_6I_3$  moiety with contentious decomposition of the donor molecule ended with a final residual carbons.

The TGA curve (Figs. 6A–6E) of [(SZ)(DDQ)] complex indicates that the mass change begins at 75 °C and continuous up to 800 °C. The first mass loss with  $DTG_{max} = 75$ , 167, 270, 327 and 355 °C corresponds to the liberation of the organic moiety  $C_5H_{11}O_3N_3S$  (obs. = 38.50%, calc. = 40.24%). The second decomposition step at 661 °C occurs in the range 400–800 °C and corresponds to the loss of  $C_4N_2O_2$  organic moiety (obs. = 22.00%, calc. = 22.48%) with continuous decomposition.

[(SS)(CHL)] was thermally decomposed in three successive decomposition steps (180, 304 and 512 °C) within the temperature range 25–800 °C. The first decomposition step (obs. = 41.46%, calc. = 41.07%) within the temperature range 25–250 °C, may be attributed to the liberation of C<sub>6</sub>H<sub>11</sub>O<sub>3</sub>N<sub>3</sub>S moiety. The second and third decomposition steps found within the temperature range 250–800 °C (obs. = 35.00%, calc. = 34.86%), which are reasonably accounted for by the removal of Cl<sub>4</sub>O<sub>2</sub> moiety. The decomposition of the SZ and CHL molecules ended with a final residue of carbon atoms.

[(SZ)(PA)] CT-complex is thermally stable up to 75 °C and decomposition beyond this temperature as indicated by the first loss step in the TG curve (Figs. 6A–6E). First step, the mass loss at 93 °C corresponds to the loss of one NO<sub>2</sub> group from PA molecule (obs. = 9.08%, calc. = 9.54%). Continuous mass loss in the TG curve from 150 to 250 °C corresponds to the loss of C<sub>5</sub>H<sub>2</sub>OH(NO<sub>2</sub>)<sub>2</sub> (obs. = 34.48%, calc. = 35.45%). The rest of SZ molecule was



**Fig. 7D.** Kinetic curves of decomposition steps of SZ/CHL CT-complex, where (CR) Coats and Redfern (CR) integral method and (HM) Horowitz and Metzger (HM) approximation method.

decomposed on three steps within the temperature range 250–800 °C corresponds to the loss of  $C_3H_{11}O_3N_3S$  (obs. = 34.75%, calc. = 35.03%). The DTG profile shows three endothermic peaks. The final decomposition of the [(SZ)(PA)] CT-complex is the residual carbon atoms.

#### 3.6. Kinetic studies

Three major different methods are used for the evaluation of kinetic parameters.

#### 3.6.1. Freeman and Carroll (FC) differential method [50]

By combining the usual first-order equation with the Arrhenius equation, one gets:

$$\ln\left[\frac{dw/dt}{w_r}\right] = \ln Z - \frac{E}{RT}$$
(8)

where *w* is the total loss in weight up to time, *t*,  $w_r = w_f - w$ ,  $w_f$  is the weight loss at the completion of the reaction, *R* is the gas constant and (dw/dt) is the weight-time gradient. A plot of  $\ln \left[\frac{dw/dt}{w_r}\right]$  against 1/T, was found to be linear. The energy of activation, *E*, was calculated from the slope and the pre-exponential factor, *Z*, was calculated from the intercept and the entropy of activation,  $\Delta S$ , was obtained from the following equation

$$\Delta S = R \ln \left(\frac{Zh}{K_B T_m}\right) \tag{9}$$

where  $K_B$ , is the Boltzmann's constant, *h* is the Planck's constant and  $T_m$ , is the DTG peak temperature.



**Fig. 7E.** Kinetic curves of decomposition steps of SZ/PA CT-complex, where (CR) Coats and Redfern (CR) integral method and (HM) Horowitz and Metzger (HM) approximation method.

### 3.6.2. Horowitz and Metzger (HM) approximation method [51] These authors derived the relation:

$$\ln[-\ln(1-\alpha)] = \frac{E}{RT_m}\Theta$$
(10)

where  $\alpha$  is the fraction of the sample decomposed at time *t* and  $\Theta = T - T_m$ .

A plot of  $\ln[-\ln(1-\alpha)]$  against  $\Theta$ , was found to be linear, Figs. 7A–7E, from the slope of which *E*, was calculated and *Z* can be deduced from the relation:

$$Z = \frac{E\varphi}{RT_m^2} \exp\left(\frac{E}{RT_m}\right) \tag{11}$$

where  $\varphi$  is the linear heating rate, the entropy of activation  $\Delta S$ , was calculated using Eq. (9). The order of reaction, *n*, can be calculated from the relation:

$$n = 33.64758 - 182.295\alpha_m + 435.9073\alpha_m^2 - 551.157\alpha_m^3 + 357.3703\alpha_m^4 - 93.4828\alpha_m^5$$
(12)

where  $\alpha_m$  is the fraction of the substance decomposed at  $T_m$ .

#### 3.6.3. Coats and Redfern (CR) integral method [52]

For first-order reactions, the Coats–Redfern equation may be written in the form:

$$\ln\left[\frac{-\ln\left(1-\alpha\right)}{T^2}\right] = \ln\left(\frac{ZR}{\varphi E}\right) - \frac{E}{RT}$$
(13)

## $\label{eq:constraint} \begin{array}{l} \textbf{Table 6} \\ \text{Kinetic parameters of SZ, } [(SZ)_2]I^+ \cdot I_3^-, \\ [(SZ)(DDQ)], \\ [(SZ)(CHL)] \text{ and } [(SZ)(PA)] \text{ CT-complexes.} \end{array}$

Method	n	Parameter						
		$\overline{E}$ (kJ mol <sup>-1</sup> )	$Z(s^{-1})$	$\Delta S (\text{J mol}^{-1} \text{K}^{-1})$	$\Delta H (\mathrm{kJ}\mathrm{mol}^{-1})$	$\Delta G (\mathrm{kJ}\mathrm{mol}^{-1})$		
SZ								
HM	1	137	$1.17\times10^{11}$	-37.9	133	153	0.9740	
CR	1	35.6	11.9	-229	31.2	153	0.9693	
$[(SZ)_2]I^+ \cdot I_3^-$								
HM	2	53.7	431	-199	49.3	156	0.9555	
CR	2	42.4	61.9	-215	38	153	0.9776	
[(SZ)(DDQ)]								
HM	3	48.6	114	-2.11	44.1	158	0.9912	
CR	3	58.1	2270	-186	53.6	154	0.972	
[(SZ)(CHL)]								
HM	1	125	$5.22\times10^{12}$	-4.98	121	124	0.9947	
CR	1	147	$1.44\times10^{15}$	-41.7	143	124	0.9931	
[(SZ)(PA)]								
HM	2	88.9	$2.69\times10^7$	-107	84.8	138	0.9927	
CR	2	107	$2.51\times10^9$	-69.2	102	137	0.9943	

n = Number of decomposition steps.

A plot of  $\ln[\frac{-\ln(1-\alpha)}{T^2}]$  against 1/T was found to be linear Figs. 7A– 7E, from the slope of which *E*, was calculated and *Z* can be deduced from the intercept. The enthalpy of activation,  $\Delta H$ , and the free enthalpy of activation,  $\Delta G$ , can be calculated via the equations:

$$\Delta H = E - RT_m; \quad \Delta G = \Delta H - T_m \Delta S \tag{14}$$

The kinetic parameters were evaluated using two of the above mentioned methods by graphical means are listed in Table 6. The satisfactory values of correlation coefficients ( $\sim$ 1) in all cases indicates good agreement with experimented data and the values of kinetic parameters are reasonable and in good agreement.

#### 4. Conclusion

The charge-transfer complexes of the sulfamethoxazole (SZ) with iodine (I<sub>2</sub>), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), *p*-chloranil (CHL) or picric acid (PA) were investigated in solid and solution cases. The molar ratio produced was found to be 1:1. The physical measurements like formation constant ( $K_{\rm CT}$ ), molar extinction coefficient ( $\varepsilon_{\rm CT}$ ), standard free energy ( $\Delta G^{\circ}$ ), oscillator strength (*f*), transition dipole moment ( $\mu$ ), resonance energy ( $R_{\rm N}$ ) and ionization potential ( $I_{\rm D}$ ) were calculated. Spectral and thermal analysis tools gave a good impression in the interpretation of sulfamethoxazole charge-transfer complexes.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.07.004.

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