Journal of Molecular Structure 983 (2010) 153–161

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Charge-transfer complexes of 1-(2-aminoethyl) piperazine with σ- and π-acceptors

Adel Mostafa, Hassan S. Bazzi *

Department of Chemistry, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar

ARTICLE INFO

Article history:
Received 26 April 2010
Received in revised form 24 August 2010
Accepted 24 August 2010
Available online 31 August 2010

Keywords:
1-(2-Aminoethyl) piperazine
Iodine
DDQ
TCNQ
TBCHD
CHL

ABSTRACT

The solid charge-transfer (CT) molecular complexes formed in the reaction of 1-(2-aminoethyl) piperazine (AEPIP) with the σ-acceptor iodine and π-acceptors 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 7,7,8,8-tetracyanoquinodi-methane (TCNQ), 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD) and 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL) were studied in chloroform at 25 °C. The products were investigated through electronic and infrared spectra as well as elemental analysis. The obtained results showed that the formed solid CT-complexes have the formulas $[(AEPIP)\ I]^+\ I_5^-$, $[(AEPIP)(DDQ)_2]$, $[(AEPIP)(TCNQ)_2]$, $[(AEPIP)_2(TBCHD)_3]$ and [(AEPIP)(CHL)] which are in full agreement with the known reaction stoichiometries in solution as well as the elemental analysis measurements. The formation constant K_{CT}, molar extinction coefficient ε_{CT}, free energy change ΔG^0 and CT energy E_{CT} have been calculated for the CT-complexes $[(AEPIP)(DDQ)_2]$, $[(AEPIP)(TCNQ)_2]$ and [(AEPIP)(CHL)] as well.

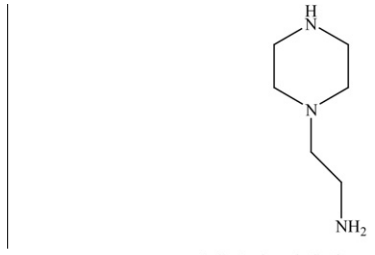
1. Introduction

The charge-transfer (CT) complexes formed in the reactions of σ- and π-electron acceptors with different donors like amines, crown ethers, polysulfur bases and oxygen–nitrogen mixed bases have been the subjects of many studies both in solution and in solid state show interesting chemical and physical properties. These properties have been the subjects of many studies both in solution and in solid state [1–10]. The photometric methods based on these interactions are usually simple and convenient because of the rapid formation of the complexes.

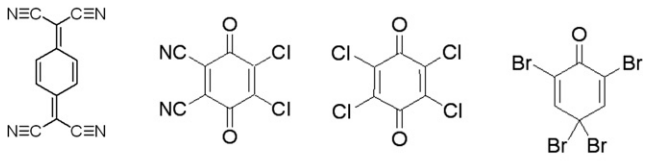
The electron donor we use in this study, 1-(2-aminoethyl) piperazine (AEPIP), is a derivative of piperazine and contains primary, secondary and tertiary nitrogen atoms (electron donating atom).

Polyiodide anions such as I_3^-, I_5^-, I_7^-, or I_9^- could be formed in charge-transfer interaction between iodine and electron donors. The formation of a particular polyiodide species depends strongly on the nature of the donor base and in some cases on the method of preparation [11–15]. The π-electron acceptors 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) are known to form stable colored CT-complexes with many donor bases. However, the reaction stoichiometries depend on several factors such as the nature of donor and acceptor and in some cases on the solvent used. The increased interest in the study of charge-transfer interactions stems from the important applications that CT-complexes can have. These include electronics, solar cells, optical devices, electrical conductivity, and others [16]. In addition, these interactions play an important role in biological systems [17].

In the paper herein, we report the formation of five new CT-complexes produced from the reaction of 1-(2-aminoethyl) piperazine with the π-acceptors 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD) and 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL) and σ-acceptor iodine in $CHCl_3$ as the solvent. The purpose of this work is to make an assessment of the correct nature and stoichiometry of each of the resulting new CT-complexes formed with each acceptor.



1-(2-Aminoethyl) piperazine (AEPIP)



TCNQ DDQ CHL TBCHD

* Corresponding author. Tel.: +974 4423 0018; fax: +974 4423 0060.
E-mail address: bazzi@tamu.edu (H.S. Bazzi).

0022-2860/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2010.08.045

2. Experimental

2.1. Materials and measurements

The chemicals were purchased from Sigma–Aldrich, USA, and used as received. The electronic absorption spectra of the $CHCl_3$ solutions of the solid CT-complexes were checked in the region 1000–250 nm using a lambda 950 Perkin Elmer UV–Vis–NIR spectrometer with quartz cell of 1.0 cm path length. Elemental analysis was done using a Perkin Elmer CHNSO elemental analyzer model 2400 series II.

Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis were carried out for all reactants and CT-complexes; using a Perkin Elmer model pyris 6 TGA computerized thermal analysis system. The rate of heating of the sample was kept at 10 °C min^{-1} under nitrogen flow at 20 ml min^{-1}. Copper sulfate pentahydrate was used as a calibration standard.

The infrared spectra of the reactants, AEPIP, DDQ, TCNQ, TBCHD and CHL (iodine has no infrared activity) and the obtained CT-complexes (KBr pellets) were recorded on a Perkin Elmer FTIR spectrometer model spectrum one.

Photometric titration measurements were performed for the reactions between the donor AEPIP and each of the acceptors iodine, DDQ, TCNQ, TBCHD and CHL in $CHCl_3$ at 25 °C in order to determine the reaction stoichiometries according to literature method [3,18]. The measurements were conducted under the conditions of fixed donor AEPIP concentrations while those of the acceptors I_2, DDQ, TCNQ, CHL or TBCHD were changed over a wide range, to produce in each case reaction solutions where the molar ratio of donor: acceptor varies from 1:0.25 to 1:4. The peak absorbancies of the formed CT-complexes were measured for all solutions in each case and plotted as a function of the acceptor to donor molar ratio. The infrared spectra of the reactants and the formed CT-complexes (KBr pellets) were recorded on a perkin-Elmer Spectrum One FTIR spectro-photometer.

2.2. Preparation of the solid CT-complexes

The five solid CT-complexes formed in the reaction of AEPIP with each of I_2, DDQ, TCNQ, TBCHD and CHL were isolated in $CHCl_3$ by drop wise addition of a saturated solution (60 ml) of the donor to a saturated solution (85 ml) of the acceptor. The resulting mixture was stirred for about 10–15 min. The mixing of reactants was associated with a strong change in color. The resulting precipitate was filtered immediately and washed several times with minimum amounts of $CHCl_3$, then dried under vacuum.

The yields of the obtained CT-complexes were 1.98 g (2.2 mmoles, 69.7%) for $[(AEPIP)I]^+I_5^-$, 2.19 g (3.8 mmoles, 63.7%) for $[(AEPIP)(DDQ)_2]$, 2.5 g (4.6 mmoles, 77.4%) for $[(AEPIP)(TCNQ)_2]$, 2.32 g (1.6 mmoles, 75.3%) for $[(AEPIP)_2(TBCHD)_3]$, and 2.13 g (5.7 mmoles, 74.7%) for [(AEPIP)(CHL)].

The complexes were characterized using spectroscopic techniques (FTIR and UV–Vis) and by elemental analysis (theoretical values are shown in brackets):

$[(AEPIP)I]^+I_5^-$ dark brown complex (M/W: 890.63 g); C, 8.11% (8.08%) H, 1.70% (1.68%); N, 4.68% (4.72%); I, 85.43% (85.52%).
$[(AEPIP)(DDQ)_2]$ dark red complex (M/W: 583.22 g); C, 45.22% (45.27%); H, 2.59% (2.57%); N, 16.77% (16.80%).
$[(AEPIP)(TCNQ)_2]$ brown complex (M/W: 537.58 g); C, 66.91% (66.97%); H, 4.24% (4.28%); N, 28.61% (28.65%).
$[(AEPIP)_2(TBCHD)_3]$ dark brown complex (M/W: 1487.5 g); C, 24.18% (24.20%); H, 2.44% (2.42%); N, 5.62% (5.65%).
[(AEPIP)(CHL)] dark brown complex (M/W: 375.08 g); C, 38.37% (38.39%); H, 4.02% (4.0%); N, 11.95% (11.98%).

3. Results and discussion

3.1. Electronic absorption spectra

Instant and strong change in color was observed upon mixing chloroform solutions of the donor AEPIP with each of the acceptor iodine, DDQ, TCNQ, TBCHD and chloranil. The colors were dark brown for AEPIP-I_2, AEPIP–TBCHD and AEPIP–CHL, dark red for AEPIP–DDQ, and brown for AEPIP–TCNQ reaction mixtures. These changes in colors clearly indicate the occurrence of the charge-transfer interactions between the donor and each of the acceptors. The electronic absorption spectra of the reactants along with those of the CT-complexes formed between the donor AEPIP and I_2, DDQ, TCNQ, TBCHD, and CHL are shown in Figs. 1–5 respectively. Strong absorption bands appeared at 365 and 290 nm for AEPIP-I_2, 731 and 531 nm for AEPIP–DDQ, 852 and 657 nm for AEPIP–TCNQ, 527 nm for AEPIP-TBCHD and 553 nm for AEPIP–CHL products.

Photometric titration measurements for the five reactions in $CHCl_3$ were performed and shown in Figs. 6–10. Interestingly, the measurements show that the donor–acceptor molar ratio is variable depending on the type of acceptor. These molar ratios were found to be 1:1 in the case of AEPIP–CHL and 1:2 in the case of AEPIP–DDQ and AEPIP–TCNQ, 1:3 in the case of AEPIP-I_2 system, and 1:1½ in case of AEPIP–TBCHD. The structures of the five new formed CT-complexes were thus formulated to be $[(AEPIP)(I_2)_3]$

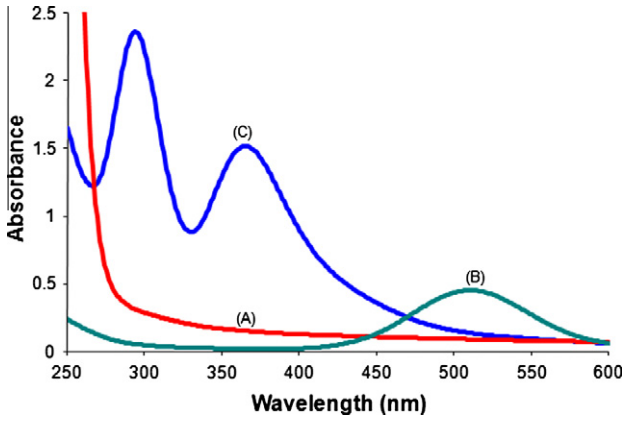


Fig. 1. Electronic absorption spectra of 1-(2-aminoethyl) piperazine (AEPIP)-I_2 in $CHCl_3$. (A) [AEPIP] = 5×10^{-3} M; (B) [I_2] = 5×10^{-3}M; (C) 1: 3 AEPIP-I_2 mixture, [AEPIP] = [I_2] = 5×10^{-3}M.

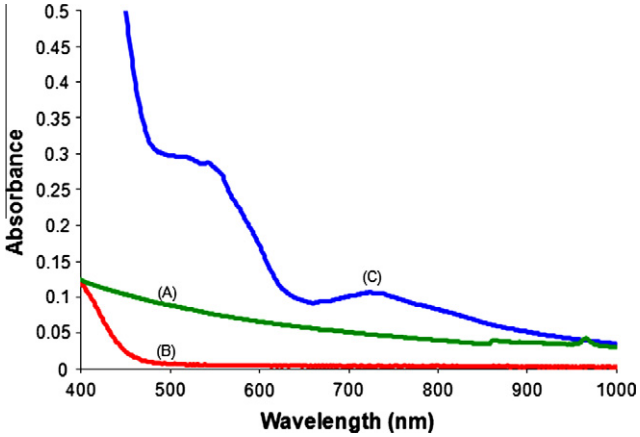


Fig. 2. Electronic absorption spectra of 1-(2-aminoethyl) piperazine (AEPIP) – DDQ in $CHCl_3$. (A) [AEPIP] = 5×10^{-3}M; (B) [DDQ] = 1×10^{-3}M; (C) 1: 2 AEPIP–DDQ mixture, [AEPIP] = 5×10^{-3}M and [DDQ] = 1×10^{-3}M.

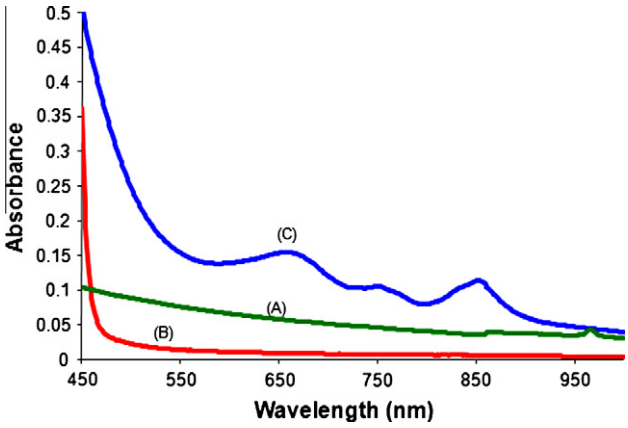


Fig. 3. Electronic absorption spectra of 1-(2-aminoethyl) piperazine (AEPIP)–TCNQ in $CHCl_3$. (A) [AEPIP] = 5×10^{-3}M; (B) [TCNQ] = 5×10^{-3}M; (C) 1: 2 AEPIP–TCNQ mixture, [AEPIP] = [TCNQ] = 5×10^{-3}M.

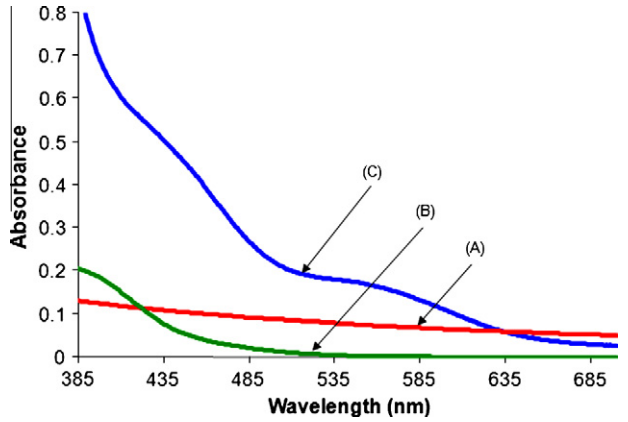


Fig. 4. Electronic absorption spectra of 1-(2-aminoethyl) piperazine (AEPIP)–TBCHD in $CHCl_3$. (A) [AEPIP] = 5×10^{-3}M; (B) [TBCHD] = 1×10^{-3}M; (C) 1:1½ AEPIP–TBCHD mixture, [AEPIP] = 5×10^{-3} M and [TBCHD] = 1×10^{-3}M.

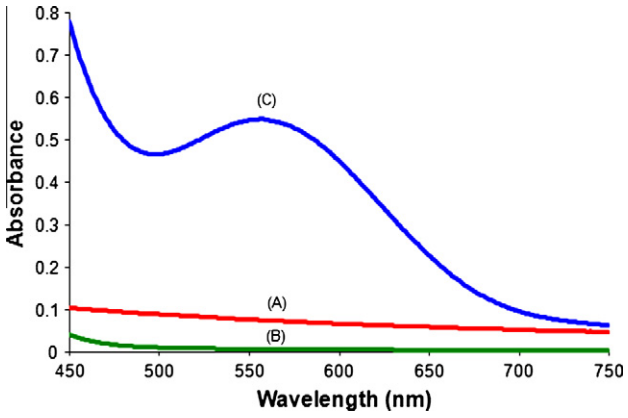


Fig. 5. Electronic absorption spectra of 1-(2-aminoethyl) piperazine) (AEPIP)–CHL in $CHCl_3$. (A) [AEPIP] = 5×10^{-3}M; (B) [CHL] = 1×10^{-3}M; (C) 1:1 AEPIP–CHL mixture, [AEPIP] = 5×10^{-3}M and [CHL] = 1×10^{-3}M.

$[(AEPIP)(DDQ)_2]$, $[(AEPIP)(TCNQ)_2]$ $[(AEPIP)_2(TBCHD)_3]$ and [(AEPIP)(CHL)].

These structures and stoichiometries agree quite well with the elemental analysis of the formed solid CT-complexes. It should

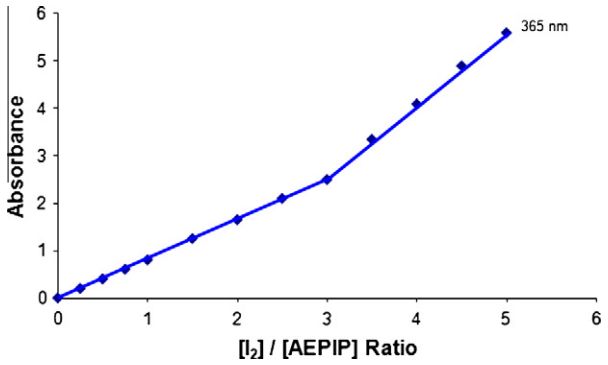


Fig. 6. Photometric titration curve for 1-(2-aminoethyl) piperazine (AEPIP) – iodine reaction in $CHCl_3$ measured at 365 nm.

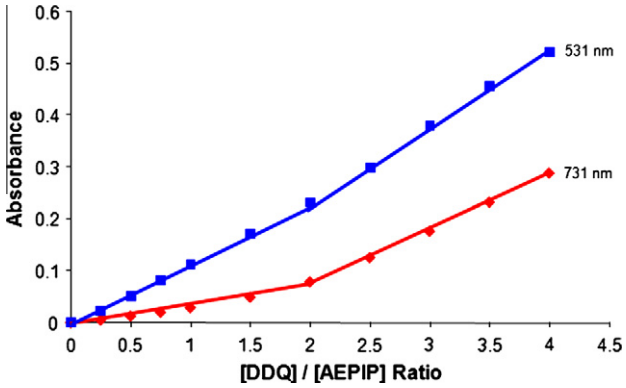


Fig. 7. Photometric titration curves for 1-(2-aminoethyl) piperazine (AEPIP)–DDQ reaction in $CHCl_3$ measured at 731 and 531 nm.

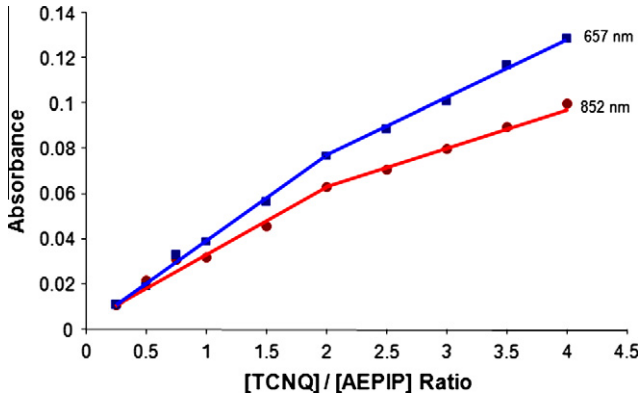


Fig. 8. Photometric titration curves for 1-(2-aminoethyl) piperazine (AEPIP)–TCNQ reaction in $CHCl_3$ measured at 852 and 657 nm.

be indicated here that the absorption of the iodine complex shows two strong absorptions at 365 and 290 nm. Neither free iodine nor AEPIP show these absorptions (Fig. 1 and Table 1). These absorptions are well known to be characteristic of the polyiodide ion of the type I_5^- [19]. Accordingly, the structure of the formed CT-complex should be $[(AEPIP)I]^+ \cdot I_5^-$ and the formation of iodide intermediate $[(AEPIP)\ I]^+ \cdot I^-$ is characterized by its known absorption at 245 nm [20]. The formation of $[(AEPIP)\ I]^+\ I_5^-$ could be understood considering the four reaction steps, the first involves the formation of the outer complex:

(i) $(AEPIP) + I_2 \rightarrow [(AEPIP)] \cdot I_2$

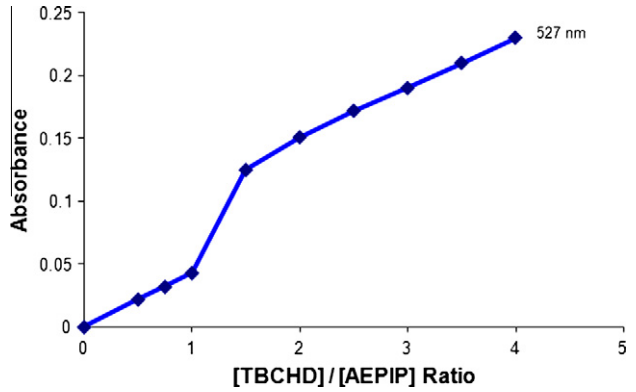


Fig. 9. Photometric titration curve for 1-(2-aminoethyl) piperazine (AEPIP)–TBCHD reaction in $CHCl_3$ measured at 527 nm.

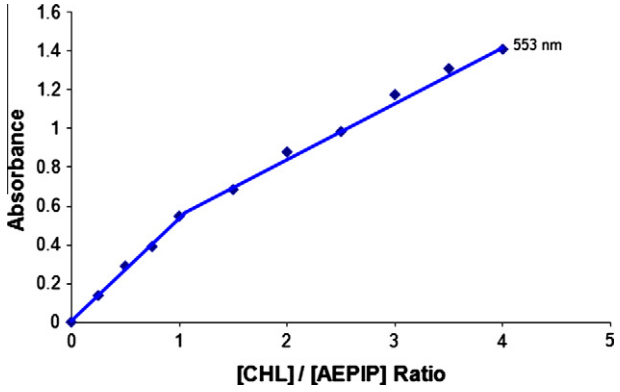


Fig. 10. Photometric titration curve for 1-(2-aminoethyl) piperazine (AEPIP)–CHL reaction in $CHCl_3$ measured at 553 nm.

Table 1
Spectroscopic data for the $CHCl_3$ solutions of CT-complexes of AEPIP with the acceptors I_2, DDQ, TCNQ, TBCHD and CHL.

Complex	Color	Absorption (nm)[a]	Stoichiometry (donor: acceptor)
[(AEPIP)I] I_5	Dark brown	365s, 290s	1:3
[(AEPIP)$(DDQ)_2$]	Dark red	731 h, 531s	1:2
[(AEPIP)$(TCNQ)_2$]	Brown	852 h, 657 m	1:2
[$(AEPIP)_2$$(TBCHD)_3$	dark brown	527sh	1:1½
[(AEPIP)(CHL)]	dark brown	553s	1:1

[a] The reactants AEPIP, Iodine, TCNQ, DDQ, TBCHD and CHL have no measurable absorptions in the wavelength region of study with used concentrations; m, medium; s, strong; sh, shoulder; h, hump.

Followed by the formation of the inner complex,

(ii) $[(AEPIP)]\cdot I_2 \rightarrow [(AEPIP)\ I]^+\cdot I^-$

The product of (ii) combines with one iodine molecule to form I_3^- which reacts with the third iodine molecule to give the final pentaiodide, I_5^-, complex.

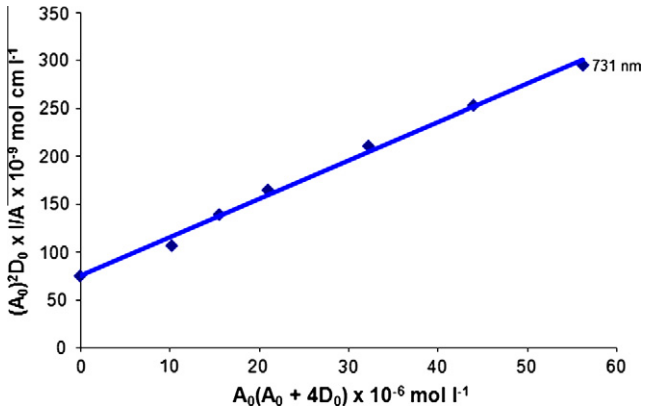


Fig. 11. Spectral determination of formation constant and molar extinction coefficient of CT-complex [(AEPIP)$(DDQ)_2$] at 731 nm.

(iii) $[(AEPIP)\ I]^+\cdot I^- + I_2 \rightarrow [(AEPIP)\ I]^+\cdot I_3^-$
(iv) $[(AEPIP)\ I]^+\cdot I_3^- + I_2 \rightarrow [(AEPIP)\ I]^+\cdot I_5^-$

It is of interest to see that the reaction stoichiometries of AEPIP with the acceptors vary from 1:1 to 1:3 depending on the type of acceptor (Table 1). For the π-acceptors, the stoichiometric ratio (AEPIP:acceptor) values are: 1:1 in the case of chloranil, 1:2 for DDQ and TCNQ, and 1:1½ for TBCHD.

These pronounced variations of CT interaction stoichiometries are definitely connected to several factors such as the donor molecular symmetry, the type of electron withdrawing groups or atoms (Cl, Br, C=O, or CN) as well as the steric hindrance between reactants. All of these factors are expected to play an important role in the electron donation process from the nitrogen electron pairs of the donor AEPIP and the aromatic ring of each acceptor.

The formation constant (K_{CT}) and molar extinction coefficient (ε_{CT}) values for the formed CT-complexes of AEPIP with DDQ, TCNQ and CHL in $CHCl_3$ at 25 °C were calculated. The 1:1 modified Benesi–Hildebrand Eq. (1) [21] was used to calculate the values of the formation constant, K_{CT} (L mol^{-1}), and the molar extinction coefficient ε_{CT} (L $mol^{-1}cm^{-1}$), for the complex [(AEPIP)(CHL)].

$$\frac{A_0 D_0 \ell}{A} = \frac{1}{k\varepsilon} + \frac{A_0 + D_0}{\varepsilon} \quad (1)$$

The corresponding spectral parameters for the complexes [(AEPIP)$(DDQ)_2$] and [(AEPIP)$(TCNQ)_2$] were calculated using the known [22] Eq. (2) of 1:2 complexes:

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

where A_0 and D_0 are the initial concentrations of the acceptor and donor, respectively, while A is the absorbancy of the mentioned CT band(s) and ℓ is the cell path length (1 cm). The data obtained via this calculation are given in Table 2. Plotting the values of $(A_0 D_0\ \ell)/A$ against $(A_0 + D_0)$ values of Eq. (1) and plotting values of $(A_0^2 D_0\ \ell)/A$ versus $A_0(A_0 + 4D_0)$ values of Eq. (2), generated straight lines with a slope of $1/\varepsilon_{CT}$ and intercept of $1/K_{CT}\ \varepsilon_{CT}$ as shown in Figs. 11–13.

Table 2
Values of K_{CT}, ε_{CT}, E_{CT} and ΔG^0 for the measured CT-complexes.

Complex	K_{CT} (L mol^{-1})	λ_{max} (nm)	$-\Delta G^0$ (cal mol^{-1})	E_{CT} (eV)	ε_{CT}/(L mol^{-1} cm^{-1})
[(AEPIP)$(DDQ)_2$]	55.45×10^3	731	6.468×10^3	1.70	0.243×10^3
[(AEPIP)$(TCNQ)_2$]	102.5×10^3	852	6.832×10^3	1.46	0.041×10^3
[(AEPIP)(CHL)]	0.369×10^3	553	3.499×10^3	2.25	0.865×10^3

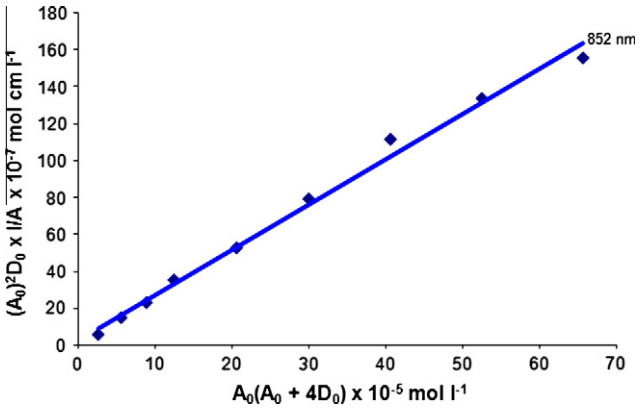


Fig. 12. Spectral determination of formation constant and molar extinction coefficient of CT-complex [(AEPIP)$(TCNQ)_2$] at 852 nm.

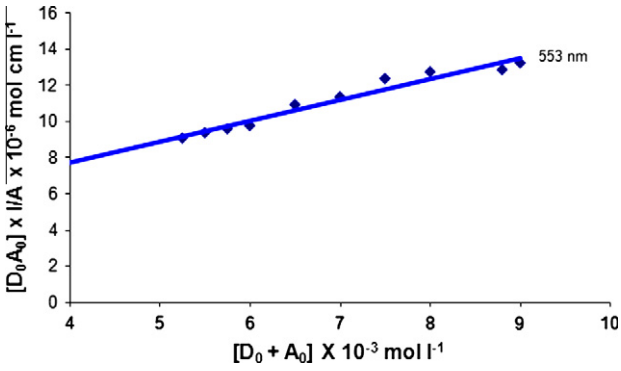


Fig. 13. Spectral determination of formation constant and molar extinction coefficient of CT-complex [(AEPIP)(CHL)] at 553 nm.

In general these complexes show high values of both the formation constant (K_{CT}) and the molar extinction coefficient (ε_{CT}). The values of K_{CT} confirm the expected high stabilities of the formed CT-complexes as a result of the expected powerful electron donation of 1-(2-aminoethyl) piperazine which contains three donor nitrogen atoms. The formation constants are strongly dependent on the nature of the used acceptors that include strong electron withdrawing groups.

The obtained data show that the CT-complex [(AEPIP)(CHL)] has much lower K_{CT} value compared with that of [(AEPIP)$(DDQ)_2$] and [(AEPIP)$(TCNQ)_2$]. The value of formation constant of

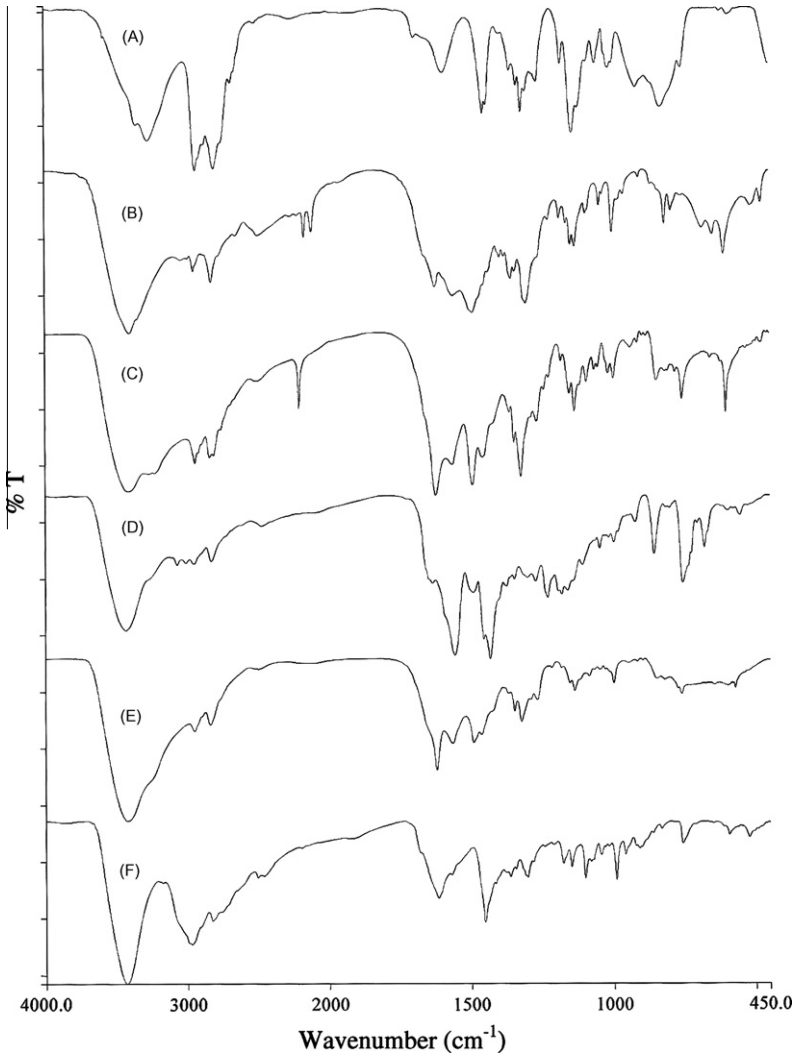


Fig. 14. Infrared absorption spectra of: (A) 1-(2-Aminoethyl) piperazine (AEPIP), (B) [(AEPIP)$(TCNQ)_2$],(C) [(AEPIP)$(DDQ)_2$], (D) [$(AEPIP)_2(TBCHD)_3$], (E) [(AEPIP)(CHL)] and (F) [(AEPIP) I]$^+$ I_5^-.

[(AEPIP)(TCNQ)$_2$] is the highest and this can be understood on the basis of the differences in the electronic structure of the acceptors TCNQ, DDQ and CHL. TCNQ has four strong withdrawing cyano groups in conjugation with an aromatic ring which causes high delocalization leading to an increase in the Lewis acidity of the acceptor.

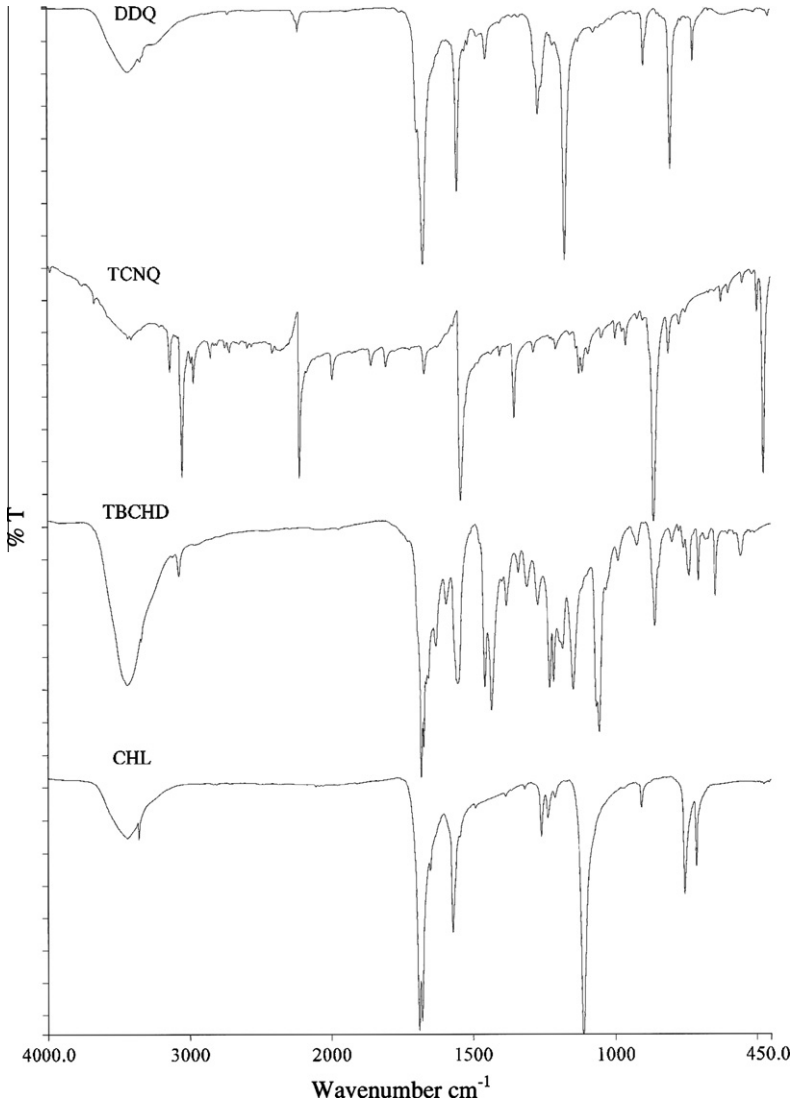


Fig. 15. Infrared absorption spectra of electron acceptors DDQ, TCNQ, TBCHD and TG.

Table 3
Infrared wavenumbers[a] (cm^{-1}) and tentative band assignments for 1-(2-aminoethyl) piperazine (AEPIP), and CT-complexes [(AEPIP)(TCNQ)$_2$], [(AEPIP)(DDQ)$_2$], [(AEPIP)$_2$(TBCHD)$_3$] [(AEPIP)(CHL)]and [(AEPIP)I] I_5.

AEPIP	[(AEPIP)(TCNQ)$_2$]	[(AEPIP)(DDQ)$_2$]	[(AEPIP)$_2$(TBCHD)$_3$]	[(AEPIP)(CHL)]	[(AEPIP) I] I_5	Assignments
3436s	3403s,br	3416s,br	3436s,br	3417s,br	3429s,br	ν (H_2O); KBr
3355s	3341w	3269w	3248w	3269w	3165w	ν(N—H); AEPIP
3270s	3039w	2944s, 2840s	2954sm, 2830m	2962sm,	2972s	ν(C—H); AEPIP
2938s	2953m, 2829sm			2839sm	2824sm	
	2269w, 2220w	2210sm				ν(C≡N); TCNQ and DDQ
		1623s	1635sm	1621s		ν(C=O); DDQ, TBCHD and CHL
	1538sm	1563sm	1596w, 1557s	1567sm		ν(C=C); TCNQ, DDQ TBCHD and CHL
1444s, 1456s	1496s, 1439w	1494s, 1458sm	1491sm, 1456s	1491sm, 141465w	1453sm	ν(CH_2); AEPIP
1361sm	1380w, 1358m	1348sm, 1324s	1374w, 1347w	1344m, 1323sm	1361m, 1302sm	Free and complexed
1337s		1306s				AEPIP
1267S1182sm	1226w, 1188m	1270sm, 1182m	1241m, 1163w	1267m, 1152w	1281w, 1178m	ν(C—N); AEPIP
1144s	1134sm	1154sm	1158w	1137m	1149m	ν(C—C); AEPIP
1091sm	1097m	1095m	1049m	1084w	1101sm	
		759sm		760sm		ν(C—Cl); CHL and DDQ

[a] m, medium; s, strong; w, weak; br, broad; ν, stretching.

An unsuccessful attempt was made to calculate the corresponding values of K_{CT} and ε_{CT} for both the 1:1½ and 1:3 complexes [(AEPIP)$_2$ (TBCHD)$_3$] and [(AEPIP)I]$^+\cdot$I$_5^-$ respectively.

The free energy change ΔG^0 (cal mol^{-1}) values of the complexes [(AEPIP)(DDQ)$_2$], [(AEPIP)(TCNQ)$_2$] and [(AEPIP)(CHL)] were calculated from Gibbs free energy of formation according to Eq. (3) [23,24] and are given in Table 2:

$$\Delta G^0 = -RT \ln K_{CT} \quad (3)$$

The obtained results of ΔG^0 reveal that the CT-complexes formation process is spontaneous. ΔG^0 values are generally more negative as the formation constants of the CT-complexes increase.

The charge transfer energy E_{CT} of the formed solid CT-complexes was calculated using: [25,26]:

$$E_{CT}(\text{nm}) = \frac{1243.667}{\lambda_{CT}} \quad (4)$$

where λ_{CT} is the wavelength of the band of the studied CT-complexes [(AEPIP)(DDQ)$_2$], [(AEPIP)(TCNQ)$_2$] and [(AEPIP)(CHL)]. The E_{CT} values calculated from Eq. (4) are listed in Table 2.

3.2. Infrared absorption spectra

The infrared absorption spectra of 1-(2-aminoethyl) piperazine (AEPIP) along with those of the formed complexes [(AEPIP)I]$^+\cdot$I$_5^-$,

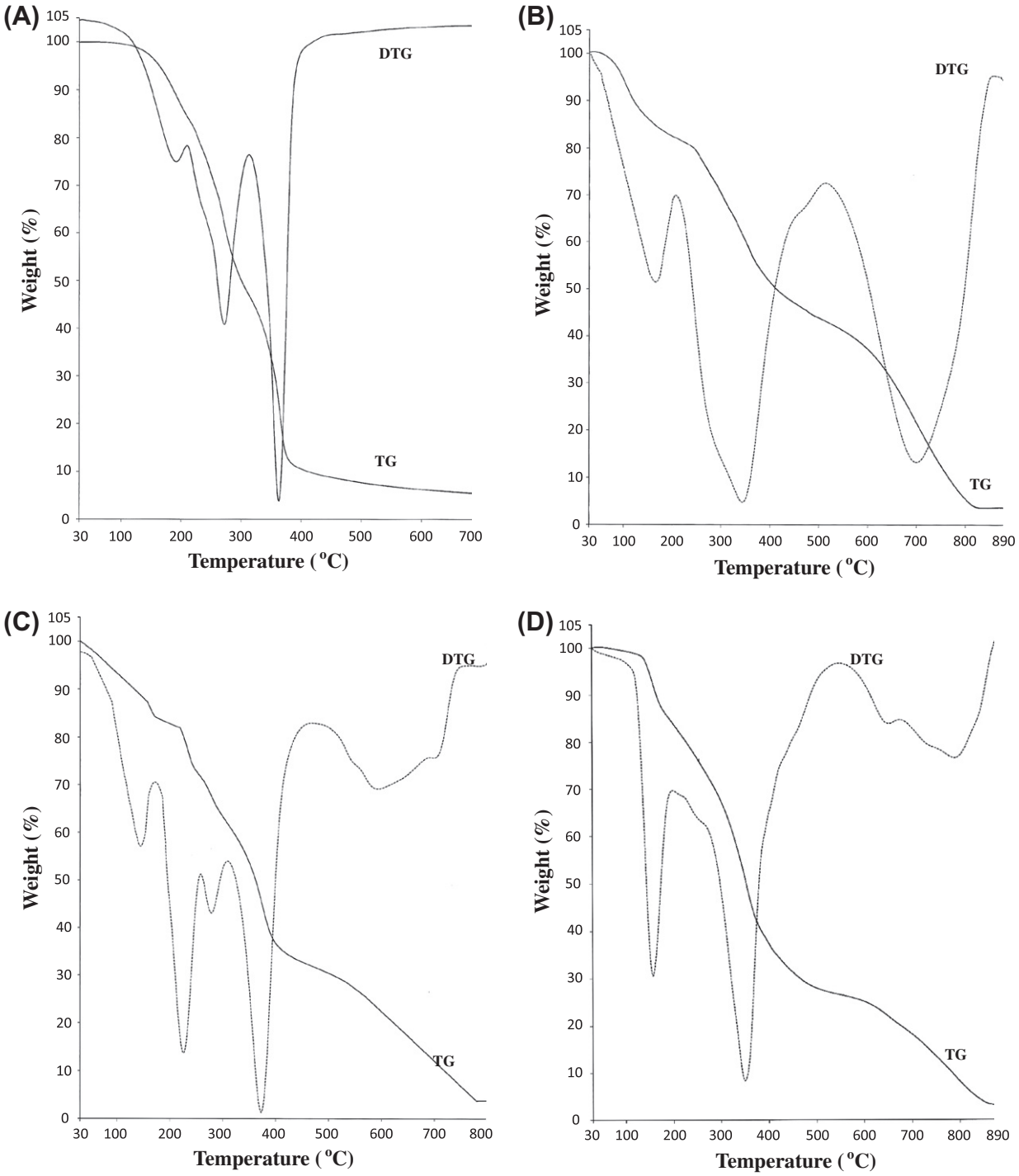


Fig. 16. Thermograms of (A) [(AEPIP) I] I$_5$, (B) [(AEPIP)(DDQ)$_2$], (C) [(AEPIP)$_2$(TBCHD)$_3$] and (D) [(AEPIP)(CHL)].

Table 4
Thermal data* for the CT-complexes [(AEPIP) I]·I_5, [(AEPIP)(DDQ)$_2$], [(AEPIP)(CHL)], [(AEPIP)$_2$(TBCHD)$_3$] and [(AEPIP)(TCNQ)$_2$].

Complex	Reaction stoichiometry donor:acceptor	DTG max (°C)	TG% mass loss found/calculated	Lost species
[(AEPIP) I]·I_5	1:3	188	14.9/14.5	AEPIP
		273	38.2/42.75	$I_2{\cdot}I^+$
		365	41.5/42.75	$I_2{\cdot}I^-$
[(AEPIP)(DDQ)$_2$]	1:2	165	18.2/22.16	AEPIP
		348, 474	40.65/38.92	DDQ } 2 DDQ
		706	39.63/38.92	DDQ }
[(AEPIP)(CHL)]	1:1	159, 248	27.1/34.45	AEPIP
	1: 1½	352	45.2/46.65	$[C_6O_2Cl_2]$ } CHL
	1:2	646,732,793	22.0/18.90	$[Cl_2]$ }
[(AEPIP)$_2$(TBCHD)$_3$]		166	16.3/17.37	2(AEPIP)
		225, 279	21.02 }	
		375	29.3 } /82.63	
		540,586, 708	28.9 }	3(TBCHD)
[(AEPIP)(TCNQ)$_2$]			Decomposed with broad decomposition peak with one maxima for a complete loss of the whole compound.	

*Thermal measurements were carried out under N_2 flow at 20 ml min^{-1}.

[(AEPIP)(DDQ)$_2$], [(AEPIP)(TCNQ)$_2$], [(AEPIP)$_2$(TBCHD)$_3$] and [(AEPIP)(CHL)] are shown in Fig. 14. Those of the electron acceptors DDQ, TCNQ, TBCHD, and CHL (I_2 has no infrared activity) are shown in Fig. 15 (the infrared band assignments are given in Table 3).

These assignments are based on the comparison of the spectra of the formed products with the spectra of the free reactants. Interestingly, the spectra of the reaction products contain the main infrared bands for both the reactants in each case. This strongly supports the formation of the donor–acceptor CT-complexes.

However, the absorptions of AEPIP and acceptors in the formed products show same changes in band intensities and in some cases small shifts in the frequency wavenumber values. These changes could be understood on the basis of the expected symmetry and electronic structure modifications in both donor and acceptor units in the formed products compared with those of the free molecules.

For example, the ν(N—H) vibrations of the free 1-(2-aminoethyl) piperazine in [(AEPIP)(DDQ)$_2$] appear at 3269 cm^{-1}, while in the [(AEPIP)(TCNQ)$_2$] two absorptions are observed at 3341 and 3039 cm^{-1} and in the [(AEPIP)I]$^+{\cdot}I_5^-$, only one absorption is observed at 3165 cm^{-1}. The outlined changes in ν(N—H) upon complexation clearly support the involvement of the nitrogen atom of the amino group in the donor AEPIP through the CT-interaction process.

It is also noteworthy that ν(C≡N) vibrations of the acceptors TCNQ and DDQ show some changes particularly in terms of band wavenumber values upon complexation. The ν(C≡N) vibration for free TCNQ is observed at 2223 cm^{-1} and for free DDQ at 2230 cm^{-1} These vibrations occur at 2269 and 2220 cm^{-1} in the spectrum of [(AEPIP)(TCNQ)$_2$] and at 2210 cm^{-1} for [(AEPIP)(DDQ)$_2$].

3.3. Thermal analysis measurements

Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis were carried out in order to confirm the decompositions and structures of the formed solid CT-complexes. Figs. 16A–D show the thermograms of [(AEPIP)I]$^+{\cdot}I_5^-$, [(AEPIP)(DDQ)$_2$], [(AEPIP)$_2$(TBCHD)$_3$] and [(AEPIP)(CHL)], respectively.

Table 4 shows the thermogravimetric data for all complexes. The data support the calculated formulas and structures of the formed CT-complexes. The degradations steps and their associated temperatures vary from one complex to another depending on the type of constituents as well as on the stoichiometries in each case. Obviously, these two factors have pronounced effects on the type of bonding, relative complex stabilities and geometries.

It is of interest to see that the pentaiodide complex [(AEPIP)I]$^+{\cdot}I_5^-$ decomposes in three degradation steps, at 188 °C corresponding to the loss of AEPIP with a weight loss of 14.9% in an agreement with the calculated value of 14.5%. This step is followed by degradation at 273 °C corresponding to the loss of [$I_2{\cdot}I^-$] species with a weight loss of 38.2% with about 4.55% deviation from the calculated value (42.75%). The third degradation step at 365 °C corresponds to the loss of another [$I_2{\cdot}I^+$] species with a weight loss of 41.5% with about 1.25% deviation from the calculated value. It is clear then that the AEPIP represents 14.5% of the complex, Table 4.

The second complex [(AEPIP)(DDQ)$_2$] decomposes at four temperatures at 165 °C corresponding exactly to the loss of the donor AEPIP with weight loss of 18.2% (22.16% calculated). The two DDQ molecules are lost at three temperatures of 348, 474 and 706 °C with total weight loss of 80.28% which is close to the calculated value of 77.84%. The deviation between the experimental and calculated values was 2.44%.

The third complex [(AEPIP)$_2$(TBCHD)$_3$] is shown in Fig. 16C. This thermogram is relatively complicated. It decomposes at seven temperatures at 166, 225, 279, 375, 540, 586 and 708 °C. The first at 166 °C shows weight loss of 16.3% corresponding to the loss of the donor AEPIP, which is very close to the calculated value of 17.37%. The other decomposition temperatures at 225, 279, 375, 540, 586 and 708 °C are associated with a total weight loss of 79.2% corresponds to the loss of the acceptor TBCHD in agreement with the calculated value of 82.63%.

The fourth complex [(AEPIP)(CHL)] shows main degradation steps, at 159, 248, 352, 646, 732 and 793 °C. The first two temperatures correspond to the loss of AEPIP and the degradations at 352, 646, 732 and 793 °C correspond to the loss of the acceptor CHL molecule. The total weight loss of those steps is 67.2% very close to the calculated value of 65.55%, Table 4. The deviation between the found and calculated values was small (1.65%).

The complex [(AEPIP)$_2$(TCNQ)$_2$] has been decomposed with broad decomposition peak with one maxima for a complete loss of the whole compound.

4. Conclusion

In conclusion, charge-transfer interactions between the donor 1-(2-aminoethyl) piperazine (AEPIP) and the σ-acceptor iodine and the π-acceptors DDQ, TCNQ, TBCHD and CHL were thoroughly studied in $CHCl_3$ at 25 °C. We were able to show that the reaction stoichiometries for the acceptors iodine, DDQ, TCNQ, TBCHD and

CHL are 1:3, 1:2, 1:2, 1:1½ and 1:1 respectively. The resulting CT-complexes were shown to have the formulas: [(AEPIP)(DDQ)$_2$],[(AEPIP)(TCNQ)$_2$], [(AEPIP)$_2$(TBCHD)$_3$], [(AEPIP)(CHL)] and $[(AEPIP)I]^{+}\cdot I_5^{-}$. Our obtained results indicate that the nitrogen atom of the amino group in the donor 1-(2-aminoethyl) piperazine (AEPIP) is involved in the complexation with the acceptors. The donor–acceptor molar ratio is different with the acceptors 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD), 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL) and iodine reactions and were found to be 1: 1½, 1:1 and 1:3 respectively. This could be related to many factors, including steric hindrance which is relatively high in the case of TBCHD and CHL. This will weaken the interaction between AEPIP and TBCHD and CHL compared with that with the other three acceptors. The aromatic rings in TBCHD and CHL have also lower electron accepting ability compared with that in other acceptors.

References

[1] R. Foster, Organic Charge Transfer Complexes, Academic Press, London, 1969. pp. 51, 387.
[2] H.S. Bazzi, A. Mostafa, S.Y. AlQaradawi, E.M. Nour, J. Mol. Struct. 842 (2007) 1.
[3] H.S. Bazzi, S.Y. AlQaradawi, A. Mostafa, E.M. Nour, J. Mol. Struct. 879 (2008) 60.
[4] L. Shahada, A. Mostafa, E.M. Nour, H.S. Bazzi, J. Mol. Struct. 933 (2009) 1.
[5] A. Mostafa, H.S. Bazzi, Spectrochim. Acta Part A 74 (2009) 180.
[6] S.Y. AlQaradawi, H.S. Bazzi, A. Mostafa, E.M. Nour, Spectrochim. Acta Part A 71 (2008) 1594.
[7] J. Casaszar, Acta Phys. Chim. 29 (1998) 34.
[8] E.M. Nour, Spectrochim. Acta Part A 167 (2000) 56.
[9] A.S.N. Murthy, A.P. Bhardwaj, Spectrochim. Acta 39A (1983) 415.
[10] S.Y. AlQaradawi, E.M. Nour, Spectrosc. Lett. 37 (2004) 337.
[11] E.M. Nour, L.H. Chen, J. Laane, J. Raman Spectrosc. 467 (1986) 17.
[12] P.J. Trotter, P.A. White, Appl. Spectrosc. 32 (1978) 323.
[13] E.M. Nour, L.A. Shahada, Spectrochim. Acta 44A (1988) 1277.
[14] W. Kiefer, H.J. Bernstein, Chem. Phys. Lett. 16 (1972) 5.
[15] G.A. Bowmaker, R.J. Knappstein, J. Chem. Soc. Dalton (1977) 1928.
[16] S. Licht, Sol. Energy Mater. Sol. Cells 35 (1995) 305.
[17] H. Salem, J. Pharm. Biomed. Anal. 29 (2002) 527.
[18] D.A. Skoog, F.J. Holler, T.A. Nieman, Principle of Instrumental Analysis, fifth ed., vol. 347, Saunders College Publishing, New York, 1992.
[19] E.M. Nour, Spectrochim. Acta 47A (1991) 743.
[20] M. Mizuno, J. Tanaka, I. Harda, J. Phys. Chem. 85 (1981) 1789.
[21] H.A. Benesi, J.H. Hildebrand, J. Am. Chem. Soc. 71 (1949) 2703.
[22] A. El-Kourashy, Spectrochim. Acta A 37 (1981) 399.
[23] M. Arslan, H. Duymus, Spectrochim. Acta A 67 (2007) 573–577.
[24] A.A.A. Boraei, Spectrochim. Acta A 58 (9) (2002) 1895.
[25] G. Briegleb, Z. Angew. Chem. 72 (1960) 401.
[26] G. Briegleb, Z. Angew. Chem. 76 (1964) 326.