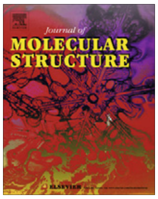
Journal of Molecular Structure 1029 (2012) 45–52

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

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



Synthesis, spectroscopic and thermal studies on solid charge-transfer molecular complexes formed in the reaction of 1-(2-aminoethyl)piperidine with π- and σ-acceptors

Adel Mostafa, G. Benjamin Cieslinski, Hassan S. Bazzi *

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

HIGHLIGHTS

- ▶ We studied the C-T reactions of the donor 1-(2-aminoethyl)piperidine with π- and σ-electron acceptors.
- ▶ We analyzed the obtained CT-complexes via FT-IR, UV-Vis, elemental and thermal analysis.
- ▶ We calculated KCT, εCT, ΔG, ECT and Ip calculated

ARTICLE INFO

Article history:
Received 10 April 2012
Received in revised form 31 May 2012
Accepted 25 June 2012
Available online 2 July 2012

Keywords:
1-(2-Aminoethyl)piperidine
Iodine
DDQ
TCNQ
TBCHD
CT-complexes

ABSTRACT

The solid charge-transfer molecular complexes formed in the reaction of the electron donor 1-(2-aminoethyl) piperidine (AEP) with the σ-acceptor iodine and π-acceptors 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD)were studied in chloroform at 25 ^{0}C. These were investigated through electronic spectra, infrared spectra, thermal and elemental analysis. The obtained results showed that the formed solid CT-complexes have the formulas $[(AEP)I]^+I_3^-$, $[(AEP)(DDQ)_2]$, $[(AEP)(TCNQ)_2]$ and $[(AEP)(TBCHD)]$ in full agreement with the known reaction stoichiometries in solution as well as the elemental measurements. The formation constant K_{CT} (L mol^{-1}), the molar extinction coefficient ε_{CT} (L mol^{-1} cm^{-1}), the free energy change $\Delta G°$ (cal mol^{-1}), the charge transfer energy E_{CT}, and the ionization potential *Ip* were calculated for the CT-complexes $[(AEP)I]^+I_3^-$, $[(AEP)(DDQ)_2]$, $[(AEP)(TCNQ)_2]$ and $[(AEP)(TBCHD)]$.

1. Introduction

The study of charge-transfer complexes formed in the reactions of σ- and π-electron acceptors with organic electron donors has considerable interest and a growing importance owing to their significant physical and chemical properties such as electrical conductivity. The chemical and physical properties of charge-transfer (CT) complexes formed in the reactions of π- and σ-electron acceptors with different donors like crown ethers amines, polysulfur bases and oxygen-nitrogen mixed bases have been the subjects of many studies both in solution and in solid state chemistry [1–10]. The electron donor used in this study, 1-(2-aminoethyl)piperidine (AEP), is a derivative of piperidine and contains both primary and tertiary nitrogen atoms (electron donating atom). It is used as a reactant for synthesis of analogs of anticancer agents.

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 [11–13]. The 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 many 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 various applications of CT-complexes, including electronics, solar cells, and optical devices [14]. These interactions play very important roles in biological systems [15]. Also, CT-complexes act as intermediates in a wide variety of reactions involving nucleophiles and electron deficient molecules.

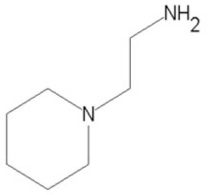
This paper reports the formation of four new CT-complexes obtained from the reaction of 1-(2-aminoethyl)piperidine (AEP) with the π-acceptors 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD), and σ-acceptor iodine

---

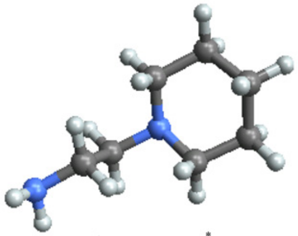
* Corresponding author. Tel.: +974 4423 0018; fax: +974 4423 0060.
E-mail address: bazzi@tamu.edu (H.S. Bazzi).

0022-2860/$ - see front matter
http://dx.doi.org/10.1016/j.molstruc.2012.06.049

(I_2) in $CHCl_3$. The aim of this study is to characterize the reaction products and make assessments of the correct nature and stoichiometry of the formed CT-complexes.

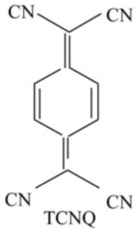


1-(2-Aminoethyl) piperidine (AEP)

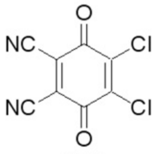


(AEP) 3D structure*

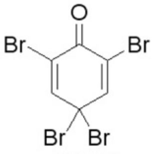
*www.wolframalpha.com



TCNQ



DDQ



TBCHD

2. Experimental

2.1. Materials and measurements

The chemicals used in this study were purchased from Sigma-Aldrich, USA, and used without further purification. The electronic absorption spectra of the $CHCl_3$ solutions of the solid CT-complexes formed in the reactions of the donor1-(2-aminoethyl)piperidine (AEP) and the acceptors iodine, 2,3-dichloro-5,6-dicyano-1, 4-benzoquinone (DDQ),7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD) as well as the reaction products were checked in the region 1000–200 nm using a Lambda 950 Perkin Elmer UV–Vis 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. The infrared spectra of the reactants, AEP, DDQ, TCNQ and TBCHD (iodine has no infrared activity) and the obtained CT-complexes (KBr pellets) were recorded on a Perkin Elmer FT-IR Spectrometer Model Spectrum One.

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 the calibration standard.

Photometric titration measurements were performed for the reactions between the donor AEP and each of the acceptors in $CHCl_3$ at 25 °C in order to determine the reaction stoichiometries according to a literature method [4,16]. The measurements were conducted under the conditions of fixed donor AEP concentrations while those of the acceptors iodine, DDQ, TCNQ, and TBCHD were changed over a wide range to produce reaction solutions where the molar ratio of donor to acceptor varied from 1:0.25 to 1:4.

The peak absorbencies of the formed CT complexes were measured for all solutions 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 Spectrum One Perkin-Elmer FT-IR Spectrophotometer.

2.2. Preparation of the solid CT-complexes

The four solid CT-complexes formed in the reaction of AEP with iodine, DDQ, TCNQ and TBCHD were prepared in $CHCl_3$ by the drop-wise addition of a saturated solution (65 ml) of each of the donors to a saturated solution (80 ml) of each of the acceptors. In each case the mixing of reactants was associated with a strong change in color. The resulting precipitate in each case was filtered off, washed with minimum amounts of $CHCl_3$ and dried in vacuum over P_2O_5. The complexes were characterized using spectroscopic techniques (FTIR and UV-vis) and by elemental analysis shown in Table 1.

3. Results and discussion

3.1. Electronic absorption spectra

Upon mixing of $CHCl_3$ solutions of iodine with the donor 1-(2-aminoethyl)piperidine (AEP), a strong change in color was observed as the solution turned into an intense dark brown color. This color, not associated with either of the reactants, indicates the existence of charge-transfer interactions between iodine and the donor. The electronic absorption spectra of the reactants along with the CT-complex formed with iodine/AEP is shown in Fig. 1.

Strong absorption bands, due to the formed product, appeared at 364 and 294 nm for AEP-I_2. Photometric titrations for the reaction in $CHCl_3$ were performed.

The molar ratio was found to be 1:2, as shown in Fig. 2. This reaction stoichiometry was supported by the obtained elemental analysis of the formed solid products. However, the two absorption bands of the formed iodine complex around 364 and 294 nm in Fig. 1, are known to be characteristics of the formation of the polyiodide ion, I_3^- [17]. Based on this, the structure of the formed CT-complex was projected as $[(AEP)I]^+I_3^-$.

The formation of the $[(AEP)I]^+$ ions is analogous to those previously reported in studies on related systems [18,19]. For example, hexamethylenetetramine (HMTA) and 1,4,7,10,13,16-hexathiacyclooctadecane (HTCOD), when reacted to iodine in $CHCl_3$ form $[(HMTA)_2I]^+I_3^-$ and $[(HTCOD)_2]^+I_5^-$. The formation of the triiodide complex $[(AEP)I]^+I_3^-$ is explained by the formation of the CT-iodide intermediate [Eq. (a)] followed by the formation of triiodide as the final product (Eq. (b)).

The formation of iodide intermediate $[(AEP)I]^+I^-$ is characterized by its absorption at 245 nm [20], particularly in experiments with a low iodine to donor ratio.

$$(AEP) + I_2 \rightarrow [(AEP)]I_2 \tag{a}$$

followed by the formation of the inner complex;

$$[(AEP)]I_2 \rightarrow [(AEP)I]^+I^-$$

which combines with one iodine molecule to form I_3^- complex

$$[(AEP)I]^+I^- + I_2 \rightarrow [(AEP)I]^+I_3^- \tag{b}$$

Fig. 3 shows the electronic spectrum recorded in the region 400–1000 nm of the reaction of DDQ with AEP. Similar to the reaction

Table 1
Elemental analysis values for the solid CT-complexes of the donor AEP with the acceptors iodine, DDQ, TCNQ and TBCHD with theoretical values in parentheses.

Name	MW (g/mol)	Color	C% (theo%)	H% (theo%)	N% (theo%)	I% (theo%)
$[(AEP)I]^+I_3^-$	635.84	Dark brown	13.18 (13.21)	2.47 (2.52)	4.42 (4.40)	79.79 (79.84)
$[(AEP)(DDQ)_2]$	582.24	Dark red	47.46 (47.40)	2.78 (2.75)	14.39 (14.43)	na
$[(AEP)(TCNQ)_2]$	536.6	Brown	69.37 (69.33)	4.49 (4.47)	26.12 (26.09)	na
$[(AEP)(TBCHD)]$	537.92	Dark brown	29.04 (29.0)	3.38 (3.35)	5.23 (5.21)	na

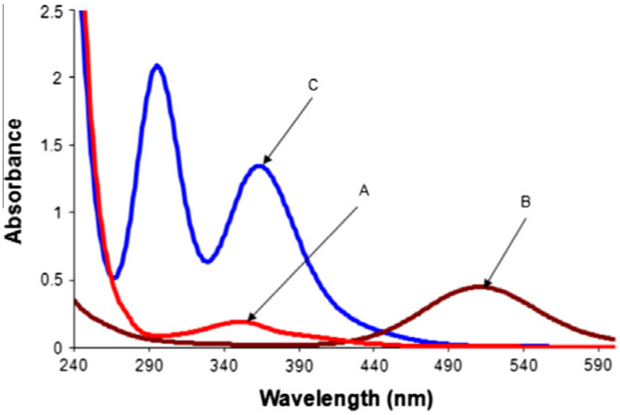


Fig. 1. Electronic absorption spectra of 1-(2-aminoethyl) piperidine (AEP)-I_2 reaction in $CHCl_3$. (A): $[AEP] = 5 \times 10^{-3}$; (B): $[I_2] = 1 \times 10^{-3}$ M; (C): 1:2 AEP-I_2 mixture, $[AEP] = 5 \times 10^{-3}$ M and $[I_2] = 1 \times 10^{-3}$ M.

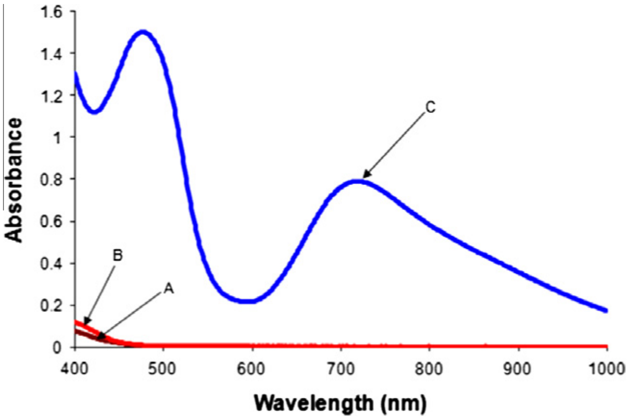


Fig. 3. Electronic absorption spectra of 1-(2-aminoethyl)piperidine (AEP)-DDQ reaction in $CHCl_3$. (A): $[AEP] = 5 \times 10^{-3}$; (B): $[DDQ] = 5 \times 10^{-3}$M; (C): 1:2 AEP-DDQ mixture, $[AEP] = [DDQ] = 5 \times 10^{-3}$ M.

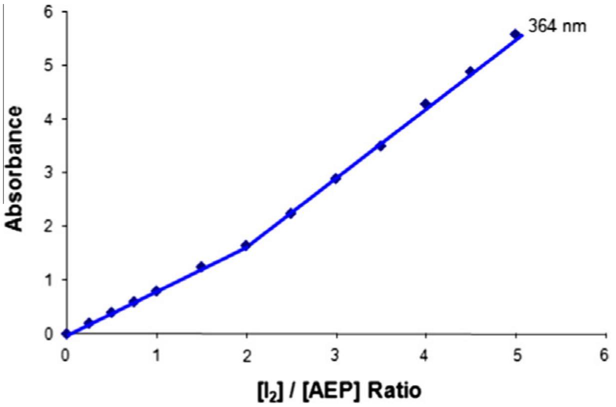


Fig. 2. Photometric titration curve for 1-(2-aminoethyl)piperidine (AEP)-iodine reaction in $CHCl_3$ measured at 364 nm.

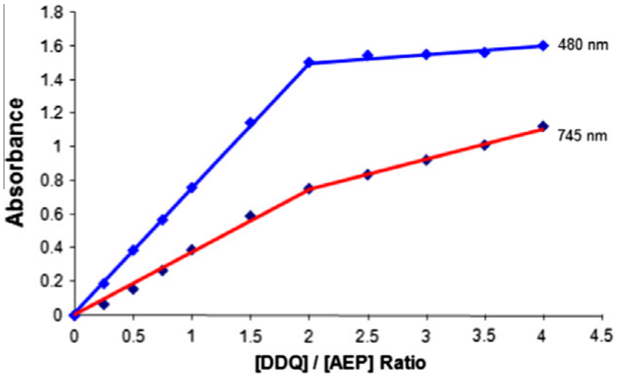


Fig. 4. Photometric titration curve for 1-(2-aminoethyl)piperidine (AEP)-DDQ reaction in $CHCl_3$ measured at 480 nm and 745 nm.

with the iodine acceptor, a strong change in color was observed upon mixing.

A dark red[1] color indicates the formation of the AEP-DDQ charge-transfer complex and is associated with the electronic transitions at 745 and 480 nm.

Photometric titration measurements were performed for AEP-DDQ reaction in $CHCl_3$ as shown in Fig. 4. The results showed that the donor-DDQ molar ratio was found to be 1:2. This is in agreement with the obtained elemental analysis of the solid CT-complex which accordingly can be formulated as $[(AEP)(DDQ)_2]$.

Fig. 5 shows the electronic absorption spectra of the reaction of TCNQ with the donor AEP. While none of the reactants' spectra display any measurable absorption in the region 450–1000 nm, the resulting CT-complex shows strong absorptions centered on 847 and 748 nm reaction. These absorptions are associated with the

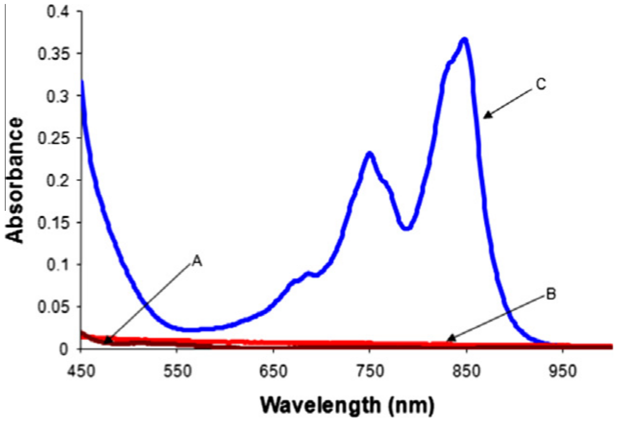


Fig. 5. Electronic absorption spectra of 1-(2-aminoethyl)piperidine (AEP)-TCNQ reaction in $CHCl_3$. (A) $[AEP] = 5 \times 10^{-3}$; (B) $[TCNQ] = 1 \times 10^{-3}$M; (C) 1: 2 AEP-TCNQ mixture, $[AEP] = 5 \times 10^{-3}$ M and $[TCNQ] = 1 \times 10^{-3}$ M.

---

[1] For interpretation of color in Figs. 1–12 and 14 the reader is referred to the web version of this article.

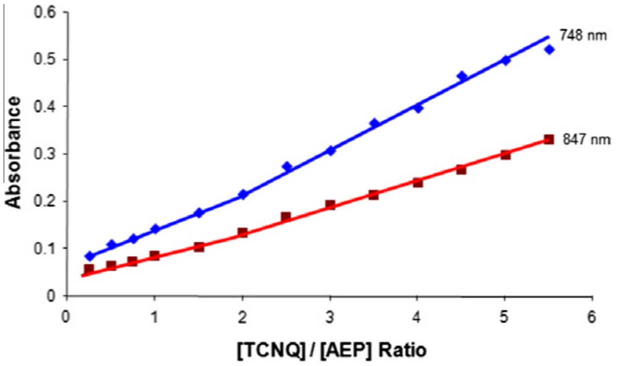


Fig. 6. Photometric titration curve for 1-(2-aminoethyl) piperidine (AEP)-TCNQ reaction in $CHCl_3$ measured at 748 nm and 847 nm.

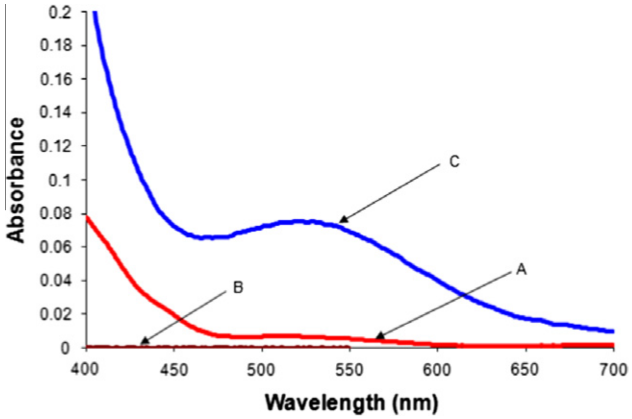


Fig. 7. Electronic absorption spectra of 1-(2-aminoethyl)piperidine (AEP)-TBCHD reaction in $CHCl_3$. (A) [AEP] = 5 × 10^{-3}; (B) [TBCHD] = 5 × 10^{-3} M; (C): 1:1 AEP-TBCHD mixture, [AEP] = [TBCHD] = 5 × 10^{-3} M.

strong color change observed upon mixing of the reactants (from a brown to a yellow solution), and reflects the electronic transitions in the formed CT-complexes.

Photometric titration measurements based on these absorptions were performed in order to determine the reaction stoichiometry in $CHCl_3$ as shown in Fig. 6. The results showed that the donor to TCNQ molar ratio was found to be 1:2. This is in agreement with the elemental analysis of the solid CT-complex. On the basis of these experimental data, the complex obtained can be formulated as $[(AEP)(TCNQ)_2]$.

Fig. 7 shows the electronic spectrum recorded in the region 400–700 nm of the reaction of TBCHD with AEP. A strong color change to dark brown was observed upon mixing and indicates the formation of the AEP-TBCHD charge-transfer complex. This complex was associated with the electronic transitions at 520 nm.

Photometric titration measurements were performed for the AEP-TBCHD reaction in $CHCl_3$ as shown in Fig. 8. The results showed that the donor-TBCHD molar ratio was found to be 1:1 and the obtained elemental analysis of the solid CT-complex accurately matched the molar ratio of 1:1 and was formulated as [(AEP)(TBCHD)]. Table 2 shows the spectroscopic data of the resulting CT-complexes.

Identification of charge transfer bands can be illustrated as follows:

The color: of CT-complexes is reflective of the relative energy balance resulting from the transfer of electronic charge from donor to acceptor.

Solvatochromism: in solution, the transition energy and therefore the complex color varies with variation in solvent permittivity, indicating variation in shifts of electron density as a result of the transition. This distinguishes it from the $\pi \rightarrow \pi^*$ transitions on the ligand.

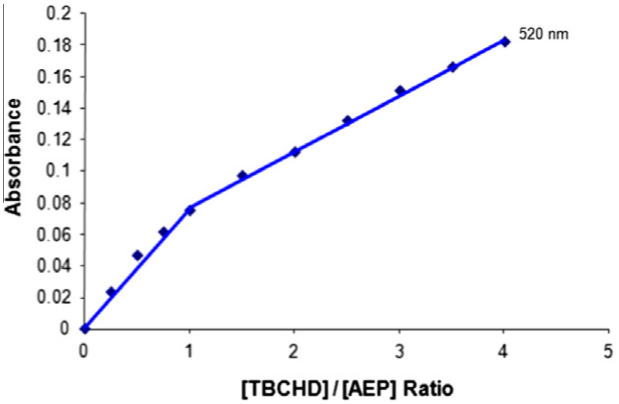


Fig. 8. Photometric titration curve for 1-(2-aminoethyl) piperidine (AEP)-TBCHD reaction in $CHCl_3$ measured at 520 nm.

Table 2

Spectroscopic data for the $CHCl_3$ solutions of solid CT-complexes of AEP with the acceptors iodine, DDQ, TCNQ and TBCHD.

Complex	Color	Absorption[a] (nm)	Stoichiometry (donor:acceptor)
$[(AEP)I]^+I_3^-$	Dark brown	364s, 294s	1:2
$[(AEP)(DDQ)_2]$	Dark red	745s, 480s	1:2
$[(AEP)(TCNQ)_2]$	Brown	847s, 748 m	1:2
[(AEP)(TBCHD)]	Dark brown	520 h	1:1

[a] The reactants AEP, iodine, DDQ, TCNQ and TBCHD have no measurable absorptions in the region of study with used concentrations; m, medium; s, strong; h, hump.

Intensity: CT absorptions bands are intense and often lie in the ultraviolet and visible portion of the spectrum.

The formation constant (K_{CT}) and molar extinction coefficient (ε_{CT}) values for the formed CT-complexes of the donor 1-(2-aminoethyl) piperidine (AEP) with iodine, DDQ, TCNQ and TBCHD in $CHCl_3$ at 25 °C were calculated.

$$\frac{A_0D_0\ell}{A}=\frac{1}{k\varepsilon}+\frac{A_0+D_0}{\varepsilon} \tag{1}$$

The 1:1 modified Benesi–Hildebrand equation (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 [(AEP)(TBCHD)].

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

The corresponding spectral parameters for the complexes $[(AEP)I]^+I_3^-$, $[(AEP)(DDQ)_2]$ and $[(AEP)(TCNQ)_2]$ were calculated using the known equation (Eq. (2)) of 1:2 complexes [22]:

Where A_0 and D_0 are the initial concentrations of the acceptors and donors, respectively, A is the absorbance of the mentioned CT bands, and ℓ is the cell path length (1 cm). The data obtained throughout this calculation is given in Table 3. Plotting the $A_0D_0\ell/A$ against $(A_0 + D_0)$ from equation (1) and plotting $(A_0)^2D_0\ell/A$ versus $A_0(A_0 + 4D_0)$ from equation (2), linear lines were obtained with a slope of $1/\varepsilon_{CT}$ and an intercept of $1/K_{CT}\varepsilon_{CT}$ as shown in Figs. 9–12.

These complexes give high values of both the formation constant (K_C) and the molar extinction coefficient (ε_{CT}). These high values of K_{CT} confirm the expected high stabilities of the formed

Table 3
Spectrophotometric and free energy results of CT-complexes of $[(\mathrm{AEP})\mathrm{I}]^+\mathrm{I}_3^-$, [(AEP)(DDQ)$_2$], [(AEP)(TCNQ)$_2$] and [(AEP)(TBCHD)] in CHCl$_3$.

Complex	K_{CT} (L mol^{-1})	λ_{max} (nm)	$-\Delta G°$ (cal mol^{-1})	E_{CT} (eV)	ε_{CT} (L mol^{-1} cm^{-1})
$[(\mathrm{AEP})\mathrm{I}]^+\mathrm{I}_3^-$	65.0×10^3	364	6.56×10^3	3.42	5.90×10^3
[(AEP)(DDQ)$_2$]	42.6×10^3	480	6.31×10^3	2.59	0.454×10^3
[(AEP)(TCNQ)$_2$]	125.3×10^3	847	6.95×10^3	1.47	0.154×10^3
[(AEP)(TBCHD)]	0.10×10^3	520	2.73×10^3	2.39	0.062×10^3

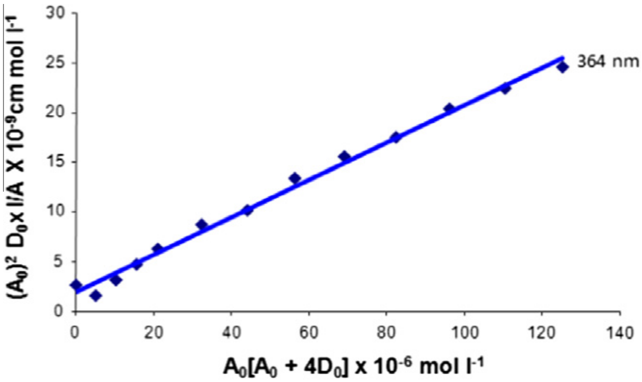


Fig. 9. Spectral determination of formation constant and molar extinction coefficient of CT-complex $[(\mathrm{AEP})\mathrm{I}]^+\mathrm{I}_3^-$ at 364 nm.

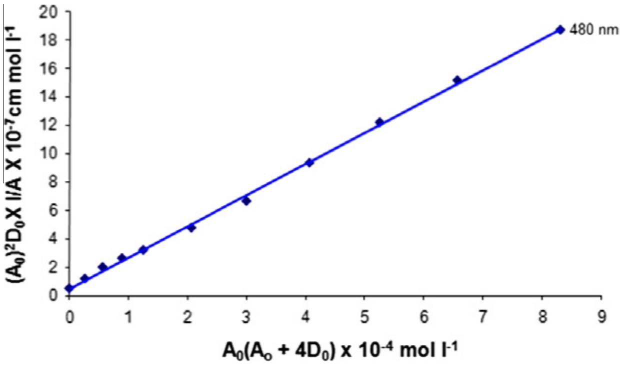


Fig. 10. Spectral determination of formation constant and molar extinction coefficient of CT-complex [(AEP)(DDQ)$_2$] at 480 nm.

CT-complexes as a result of the expected high donation of 1-(2-aminoethyl) piperidine. The formation constants are strongly dependent on the nature of the used acceptors including the type of electron withdrawing substituent.

The obtained data shows that the CT-complex [(AEP)(TBCHD)] has a much lower value of K_{CT} compared with that of [(AEP)(DDQ)$_2$], [(AEP)(TCNQ)$_2$] and $[(\mathrm{AEP})\mathrm{I}]^+\mathrm{I}_3^-$. This demonstrates a much higher stability of these three complexes compared with TBCHD. This could be related to several factors. First, the steric hindrance is relatively high in the case of TBCHD due to the larger atomic size of the bromine substituent compared with the chlorine in DDQ. Also, TCNQ has four cyano groups which are strong electron withdrawing groups. Second, the aromatic ring in TBCHD has a lower electron accepting ability compared to DDQ or TCNQ, related to the lower electron withdrawing process of the substituent bromine in TBCHD compared to chlorine in DDQ. This allows for stronger electron donation from the AEP base to the three acceptors, DDQ, TCNQ and iodine, compared with TBCHD.

The CT-complex $[(\mathrm{AEP})\mathrm{I}]^+\mathrm{I}_3^-$ shows the highest value of both K_{CT} and ε_{CT}. The high value of K_{CT} reflects the high stability of the

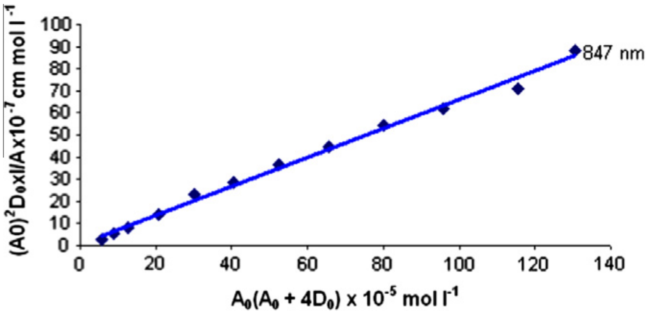


Fig. 11. Spectral determination of formation constant and molar extinction coefficient of CT-complex [(AEP)(TCNQ)$_2$] at 847 nm.

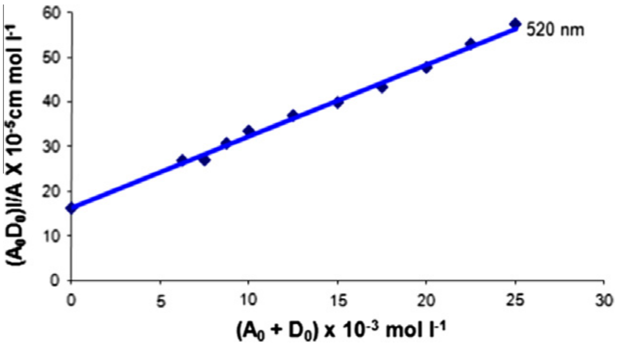


Fig. 12. Spectral determination of formation constant and molar extinction coefficient of CT-complex [(AEP)(TBCHD)] at 520 nm.

iodine complex. As a result of the expected strong donation of AEP, the high value of ε_{CT} agrees with the existence of the triiodide ion, I_3^-, which is known to have a high absorptivity value [23,24].

The free energy change $\Delta G°$ (cal mol^{-1}) values of the complexes $[(\mathrm{AEP})\mathrm{I}]^+\mathrm{I}_3^-$, [(AEP)(TCNQ)$_2$], [(AEP) (DDQ)$_2$] and [(AEP)(TBCHD)] were calculated from Gibbs free energy of formation according to Eq. (3) [25,26]:

$$\Delta G^\circ = -\mathrm{RT}\ln K_{CT} \tag{3}$$

where $\Delta G°$ is the free energy of the charge transfer complexes; R the gas constant (1.987 cal mol^{-1} °C); T the temperature in Kelvin, and K_{CT} the formation constant of donor–acceptor complexes (L mol^{-1}).

The $\Delta G°$ values of the complexes are given in Table 3. The obtained results of $\Delta G°$ reveal that the CT-complexes formation process is exothermic in nature and spontaneous.

The results of $\Delta G°$ are generally more negative as the formation constants of the CT-complexes increase. As the bond between the components becomes stronger and thus the components are subjected to more physical strain or loss of freedom, the values of $\Delta G°$ become more negative. The more negative the value for $\Delta G°$, the farther to the right the reaction will proceed in order to achieve equilibrium.

The charge transfer energy E_{CT}: there is a corresponding relation between the amount of transferred charge and the change of the energy originating from charge transfer. As the amount of transferred charge increases, the total energy decreases and the luminescence intensity increases. Therefore the energy of charge transfer from guest to host may be derived from the charge transfer. E_{CT} of the formed solid CT-complexes was calculated using the following equation (4) [27,28]:

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

where λ_{CT} is the wavelength (nm) of the studied CT-complexes $[(AEP)I]^+I_3^-$, $[(AEP)(DDQ)_2]$, $[(AEP)(TCNQ)_2]$ and $[(AEP)(TBCHD)]$. The E_{CT} values calculated from equation (4) are listed in Table 3. These results (K_{CT}, ε_{CT}, ΔG° and E_{CT}) explain that the obtained solid CT-complexes formed in the reaction of the donor AEP and the acceptors iodine, TCNQ, DDQ and TBCHD have high CT energy and formation constants (K_{CT}).

The ionization potential is the difference in potential between the initial state, in which the electron is bound, and the final state, in which it is at rest of infinity, can be determined from the CT energies of the CT band of the complexes. For the acceptors iodine, DDQ, TCNQ and TBCHD, the relationship becomes the following [27–29]:

$$E_{CT} = Ip - 5.2 + \frac{1.5}{Ip - 5.2} \quad (5)$$

where Ip is the ionization potential (eV) and E_{CT} is the charge transfer energy of the formed solid CT-complexes. The obtained values of ionization potential are 6.9, 6.5, 5.6 and 6.4 eV for the obtained CT-complexes $[(AEP)I]^+I_3^-$, $[(AEP)(DDQ)_2]$, $[(AEP)(TCNQ)_2]$ and $[(AEP)(TBCHD)]$, respectively. It has been reported that the ionization potential of the electron donor may be correlated with the charge transfer transition energy of the complex [30].

3.2. Infrared absorption spectra

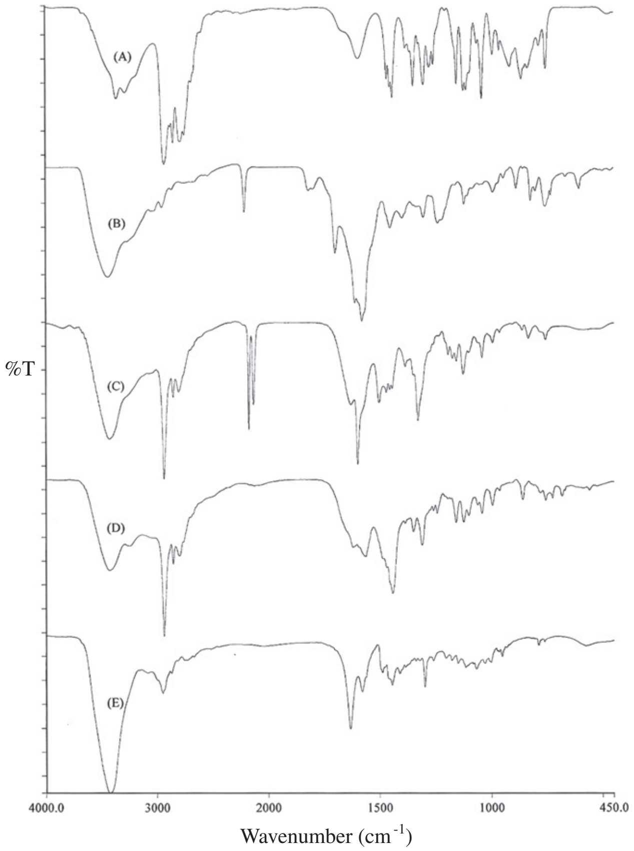


Fig. 13. Infrared absorption spectra of: (A) 1-(2-aminoethyl) piperidine (AEP), (B) $[(AEP)(DDQ)_2]$, (C) $[(AEP)(TCNQ)_2]$, (D) $[(AEP)(TBCHD)]$, and (E) $[(AEP)I]^+I_3^-$.

The infrared absorption spectra of the donor 1-(2-aminoethyl) piperidine (AEP) along with those of the formed complexes $[(AEP)I]^+I_3^-$, $[(AEP)(DDQ)_2]$, $[(AEP)(TCNQ)_2]$ and $[(AEP)(TBCHD)]$ are shown in Fig. 13. The infrared band assignments are given in Table 4. These assignments are based on the comparison of the spectra of the formed products with the spectra of the free reactants, the donor AEP and the acceptors iodine, DDQ, TCNQ and TBCHD.

The spectra of the reaction products contain the main infrared bands for both AEP and each of the accepting reactants. This supports the formation of the donor-acceptor CT-complexes. However,

Table 4
Infrared wavenumbers (cm^{-1}) and tentative band assignments for AEP, $[(AEP)(DDQ)_2]$, $[(AEP)(TCNQ)_2]$, $[(AEP)I]^+I_3^-$ and $[(AEP)(TBCHD)]$.

[AEP]	$[(AEP)(DDQ)_2]$	$[(AEP)(TCNQ)_2]$	$[(AEP)I]^+I_3^-$	$[(AEP)(TBCHD)]$	Assignments
3363s	3437s	3422s	3417s	3429s	$\nu(H_2O)$; KBr
3285m	3263w	3280w	3082w	3242w	ν(N—H); AEP
3192w					
2928s	3021w	2928s	2945m	2928s	ν(C—H); AEP
2285s	2956w	2854m	2868w	2854m	
	2215m	2746ms			$\nu(C{\equiv}N)$; DDQ,TCNQ
		2134ms			
	1699ms			1635m	ν(C=O); DDQ, TBCHD
	1574s	1598s		1563m	ν(C=C); DDQ, TBCHD, TCNQ
1382w	1396m	1383m	1338w	1383w	Free and complexed AEP
1346ms	1349w	1347w	1319w	1349m	
1277ms	1239ms	1243w	1297ms	1256w	ν(C—N); AEP
	1220w	1156m	1256w	1242w	
1154ms	1160w	1171w	1174w	1157m	ν(C—C); AEP
1124ms	1121m	1126m	1147w	1123m	
1041ms	1083w	1041m	1028w	1041m	
992ms	990m	994m	998w	994m	δ(CH)deformation, AEP
963m	968w	963w	965w	963w	
864ms	888m	861w	870w	859m	δ(CH); out of plan
784m	798w		784w		Wag; AEP
754ms	756ms	755w	757w	757w	NH deform-ation

m, medium; s, strong ; w, weak; br, broad; ν, stretching; δ, bending.

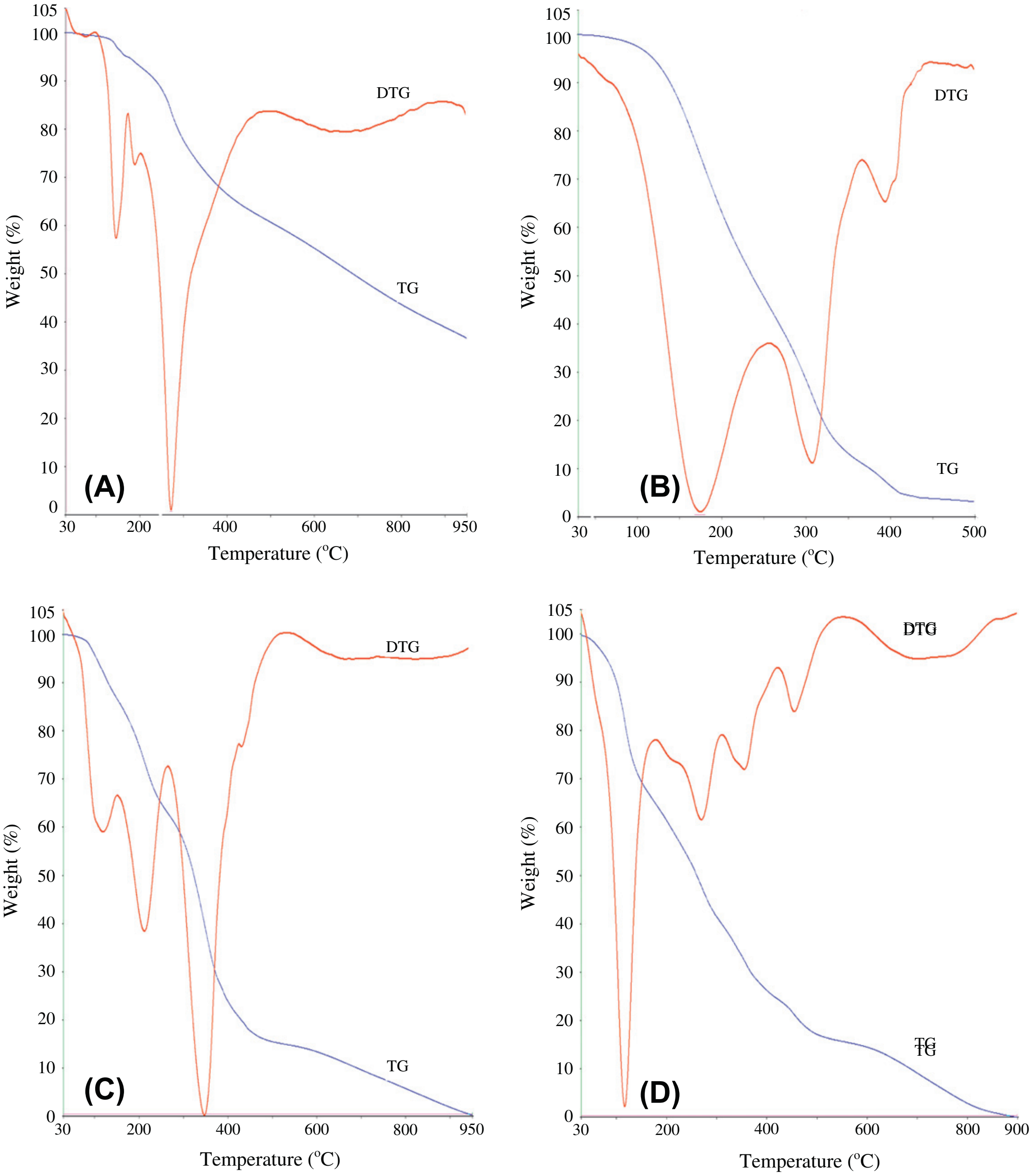


Fig. 14. (A–D) Thermograms of the CT- complexes; (A) [(AEP)(DDQ)$_2$], (B) $[(AEP)I]^+I_3^-$, (C) [(AEP)(TBCHD)] and (D) [(AEP)(TCNQ)$_2$].

Table 5
Thermal data for the CT-complexes $[(AEP)I]^+I_3^-$, [(AEP)(DDQ)$_2$], [(AEP)(TCNQ)$_2$], and [(AEP)(TBCHD)].

Complex	Reaction stoichiometry donor:acceptor	DTG max (°C)	TG% mass loss found/ calculated	Lost species
$[(AEP)I]^+I_3^-$	1:2	174	56.0/60.1	[(AEP)I$_2$]
		308, 392, 407	39.3/39.9	(I$_2$)
[(AEP)(DDQ)$_2$]	1:2	145, 187, 272	37.9/38.5	[AEP, CN, Cl$_2$]
		681	20.8/22.3	[C_7NO_2]
		950		Uncertain with 39.2% carbon decomposition residue
[(AEP)(TCNQ)$_2$]	1:2	122	34.3/33.6	[(AEP)(CN)$_2$]
		205, 270, 335, 360, 455, 708	65.7/66.4	[TCNQ], [$C_{10}H_4N_2$]
[(AEP)(TBCHD)]	1:1	126, 213	34.18/36.85	[(AEP)(Br)]
		349, 387, 421, 654, 855	62.8/63.1	[$C_6H_2Br_3O$]

the absorptions of AEP and acceptors in the formed products show changes in band intensities and some small shifts in the frequency wavenumber values. These changes may be explained by 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 AEP in $[(AEP)(DDQ)_2]$are at 3263 and 3054 cm^{-1} while in the $[(AEP)(TCNQ)_2]$ and $[(AEP)I]^+I_3^-$, one absorption is only observed in each case at 3280 and 3082 cm^{-1}, respectively.

The outlined changes in ν(N—H) upon complexation support the involvement of the nitrogen atom of the amino group in the donor AEP through the CT-interaction process. It may indicate that the ν(C≡N) vibrations of the acceptors TCNQ and DDQ change 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 2134 and 2176 cm^{-1} in the spectrum of $[(AEP)(TCNQ)_2]$ and at 2215 cm^{-1} for$[(AEP)(DDQ)_2]$.

3.3. Thermal analysis measurements

Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis were carried out under a N_2 flow (20 ml min^{-1}) in order to confirm the formulas and structures of the four solid CT-complexes. Fig. 14A–D show the thermograms of $[(AEP)(DDQ)_2]$, $[(AEP)I]^+I_3^-$, [(AEP)(TBCHD)] and $[(AEP)(TCNQ)_2]$ respectively.

The thermogravimetric data for these complexes is shown in Table 5. The obtained 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 their stoichiometry. These two factors have pronounced effects on the type of bonding, relative complex stabilities and geometries.

The first CT-complex $[(AEP)(DDQ)_2]$ shown in Fig. 14A decomposes in four temperature steps at 145, 187, and 272 °C corresponding to the loss of $[(AEP)(CN)(Cl_2)]$ with total weight loss of 37.9% (38.5% calculated) and at 681 °C corresponds to loss of [C7NO2] with weight loss of 20.8 % (22.3% calculated). The lost species are not certain at 950 °C because the complex loss is not complete with a carbon residue of 39.2% by weight at that temperature. The combustion of the complex was performed under an inert atmosphere of nitrogen gas.

It is interesting to see that the triiodide complex $[(AEP)I]^+I_3^-$ shown in Fig. 14(B) decomposes in four degradation steps. The loss at 174 °C corresponds to the loss of $[(AEP)I]^+I^-$ with a weight loss of 56% very close to the calculated value of 60.1%. This step is followed by three degradations at 309, 392 and 407 °C corresponding to the loss of $[I_2]$ species with a total weight loss of 39.3% with a 0.6% deviation from the calculated value (39.9%). This is evident that the AEP represents 20.16% of the complex, Table 5.

The third complex [(AEP)(TBCHD)] is shown in Fig. 14C. This thermogram is relatively complicated. It decomposes at seven temperatures at 126, 213, 349, 387, 421, 654 and 855 °C. The temperatures of 126 °C and 213 °C show total weight loss of 37.18% corresponding to the loss of the donor with one bromine atom [(AEP)(Br)] species very close to the calculated value of 36.85%. The other decomposition temperatures at 349, 387, 421, 654 and 855 °C are associated with a total weight loss of 62.82% corresponding to the loss of the acceptor losing one bromine atom in the first two decomposition steps at temperatures 126 °C and 213 °C$[C_6H_2Br_3O]$in agreement with the calculated value of 63.15%.

The fourth complex $[(AEP)(TCNQ)_2]$ shown in Fig. 14(D) has six main degradation steps at 122, 205, 270, 360, 455 and 708 °C. The temperature 122 °C corresponds to the loss of $[(AEP)(CN)_2]$ with a weight loss of 34.3% very close to the calculated value of 33.6%. The temperatures of 205, 270, 335, 360, 455 and 708 °C correspond to the loss of the acceptor $[TCNQ + C_{10}H_4N_2]$. The total weight loss of those steps is 65.7%, close to the calculated value of 66.4% as shown in Table 4. The deviation between the observed and calculated values was small (0.7%).

4. Conclusion

Charge-transfer interactions between the donor AEP, the σ-acceptor iodine, and the π-acceptors DDQ, TCNQ and TBCHD were studied in $CHCl_3$ at 25 °C. We were able to show that the reaction stoichiometry is the same for the acceptors DDQ, TCNQ and iodine (1:2) but differ with TBCHD which is 1:1; the resulting CT-complexes were shown to have the formulas $[(AEP)I]^+I_3^-$, $[(AEP)(DDQ)_2]$, $[(AEP)(TCNQ)_2]$, and [(AEP)(TBCHD)]. Our results indicate that the nitrogen atom of the amino group in the donor AEP is involved in the complexation with the acceptors. The measurements show the donor-acceptor molar ratio differs only with the acceptor (TBCHD) reaction and were found to be 1:1. This could be due to multiple factors. First, the steric hindrance is relatively high in the TBCHD due to the larger substituent bromine atomic size compared that of chlorine in DDQ. This will weaken the interaction between AEP and TBCHD compared with that with the other three acceptors. Second, the aromatic ring in TBCHD has lower electron accepting ability and a lower electron withdrawing process of the substituent bromine in TBCHD compared with the other acceptors. This allows stronger electron donation from AEP base to iodine, DDQ, and TCNQ compared to TBCHD.

References

[1] R. Foster, Organic Charge Transfer Complexes, Academic Press, London, 1969. pp. 51 and 387.
[2] A. Mostafa, H.S. Bazzi, Spectrochim. Acta Part A 74 (2009) 180.
[3] A. Mostafa, H.S. Bazzi, Spectrochim. Acta Part A 79 (2011) 1613.
[4] H.S. Bazzi, A. Mostafa, S.Y. AlQaradawi, E.M. Nour, J. Mol. Struct. 842 (2007) 1.
[5] H.S. Bazzi, S.Y. AlQaradawi, A. Mostafa, E.M. Nour, J. Mol. Struct. 879 (2008) 60.
[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, Spetrochim. 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] S. Licht, Sol. Energy Mater. Sol. Cells 35 (1995) 305.
[15] H. Salem, J. Pharm. Biomed. Anal. 29 (2002) 527.
[16] D.A. SKoog, Principle of Instrumental Analysis, Sunder College Publishing, New York, 1985 (Chapter7).
[17] W. Kiefer, H.J. Bernstein, Chem. Phys. Lett. 16 (1972) 5.
[18] G.A. Bowmaker, R.J. Knappstein, J. Chem. Soc. Dalton (1977) 1928.
[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] L. Andrews, E.S. Prochaska, A. Loewenschuss, Inorg. Chem. 19 (1980) 463.
[24] K. Kaya, N. Mikami, Y. Udagawa, M. Ito, Chem. Phys. Lett. 16 (1972) 151.
[25] M. Arslan, H. Duymus, Spectrochim. Acta A 67 (2007) 573–577.
[26] A.A.A. Boraei, Spectrochim. Acta A 58 (9) (2002) 1895.
[27] G. Briegleb, Z. Angew. Chem. 72 (1960) 401.
[28] G. Briegleb, Z. Angew. Chem. 76 (1964) 326.
[29] Moamen S. Refat, Akram M. El-Didamony, Ivo Grabchev, Spectrochim. Acta A 67 (2007) 58.
[30] M. Pandeeswaran, K.P. Elango, Spectrochim. Acta A 65 (2006) 1148.