Spectroscopic characterization of charge transfer complexes of 2,3-diaminopyridine with chloranilic acid and dihydroxy-p-benzoquinone in polar solvent

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Spectroscopic characterization of charge transfer complexes of 2,3-diaminopyridine with chloranilic acid and dihydroxy-*p*-benzoquinone in polar solvent

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HIGHLIGHTS

- CT-complexes between 2,3-DAP with CHA and DHBQ were studied spectrophotometrically.
- Minimum–maximum absorbance method has been used for estimating the formation constants of the charge transfer reactions (K_{CT}).
- The charge transfer energy of the formed complexes was reached acceptable values suggesting the stability of the formed CT-complexes.

GRAPHICAL ABSTRACT

Computed ^{1}H NMR spectrum of 2,3-DAP-CHA charge transfer complex.
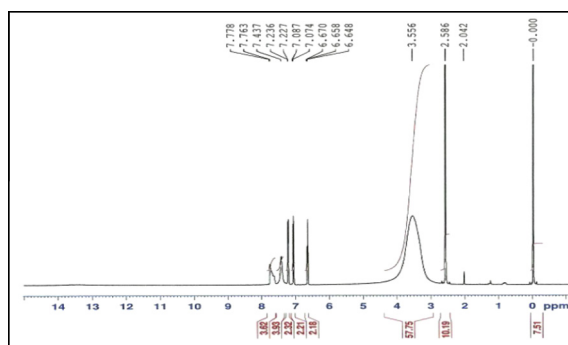
ARTICLE INFO

ABSTRACT

Charge transfer (CT) complexes formed between 2,3-aminopyridine (2,3-DAP) as electron donor with the π-electron acceptors chloranilic acid (CHA) and dihydroxy-*p*-benzoquinone (DHBQ) were investigated spectrophotometrically in ethanol. Minimum–maximum absorbance method has been used for estimating the formation constants of the charge transfer reactions (K_{CT}). Job's method of continuous variation and photometric titration studies were used to detect the stoichiometric ratios of the formed complexes and they showed that 1:1 complexes were produced. The molar extinction coefficient (ε), oscillator strength (f), dipole moment (μ), charge transfer energy (E_{CT}), ionization potential (I_P) and the dissociation energy (W) of the formed complexes were estimated, they reached acceptable values suggesting the stability of the formed CT-complexes. The solid CT-complexes were synthesized and characterized by elemental analyses, ^{1}H NMR and FTIR spectroscopies where the formed complexes included proton and electron transfer.

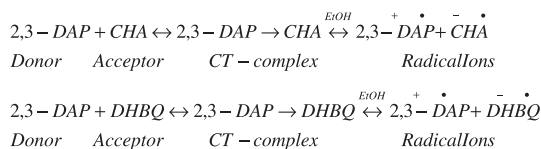© 2013 Elsevier B.V. All rights reserved.

Introduction

Proton or electron transfer complexes play an important role in the field of magnetic, electrical conductivity and optical properties [1–5]. A great number of charge transfer receptors have been reported under the basic construction strategy of employing hydrogen bonding [6–8]. Generally, CT-interaction between benzoquinones electron acceptors and electron donors containing nitrogen, oxygen or sulfur atoms has been reported over the last years. These types of interactions play an important role in the field of drug-receptors binding mechanism [9,10], surface chemistry [11], applications in solar energy storage [12], uses as organic superconductors [13], and in many biological fields as antibacterial

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$$2,3-DAP + CHA \leftrightarrow 2,3-DAP \xrightarrow{EtOH} CHA \leftrightarrow 2,3-\overset{+}{D}\overset{\bullet}{A}P + \overset{\bullet}{C}\overset{-}{H}A$$
Donor   Acceptor   CT − complex   RadicalIons

$$2,3-DAP + DHBQ \leftrightarrow 2,3-DAP \xrightarrow{EtOH} DHBQ \leftrightarrow 2,3-\overset{+}{D}\overset{\bullet}{A}P + \overset{\bullet}{D}\overset{-}{H}BQ$$
Donor   Acceptor   CT − complex   RadicalIons

Scheme 1. Formation of CHA and DHBQ radical anion.

and antifungal agents [14–16] and have a good antibacterial, anti-microbial and antifungal activities [17–21].

Aminopyridines are bioactive N-heterocyclic amines, which increase the strength of the nerve signal by blocking of the voltage dependent K^+ channel [22,23]. Also, aminopyridines have been proposed as drugs for the treatment of many diseases such as myocardial infarction as antithrombus agents and diarrhea as antimicrobial agents [24–26]. Moreover, aminopyridines are commonly present in synthetic and natural products [27]. They form repeated moiety in many large molecules with interesting photophysical, electrochemical and catalytic applications [28].

In connection with our work on electron or proton transfer complexes [29–34], and due to the biological and pharmaceutical applications of aminopyridines, this article presents our results on spectroscopic studies of the charge transfer complexes between 2,3-aminopyridine with chloranilic acid and dihydroxy-*p*-benzo-quinone (Scheme 1), in ethanol. The molecular composition of the complexes were studied using Job's and photometric titration methods. The formation constant (K_{CT}), molar extinction coefficient (ε), standard free energy change ($\Delta G°$), oscillator strength (f), transition dipole moment (μ), ionization potential (I_P) and dissociation energy (W) of the formed CT-complexes were estimated and evaluated. In addition, the solid CT-complexes were isolated and characterized using elemental analyses, infrared and ^{1}H NMR measurements.

Experimental

Chemicals

All chemicals used were of analytical grade. 2,3-aminopyridine (2,3-DAP) was supplied by Acros Organics, chloranilic acid (CHA) and 2,5-dihydroxy-*p*-benzoquinone (DHBQ) were supplied by Fluka. Ethanol (EtOH) was purchased from PAI-ACS. KBr was spectroscopic grade supplied by Aldrich.

Physical measurements

Electronic spectra
The electronic spectra were recorded in the region 700–250 nm using UV–Vis Shimadzu UV-1800 spectrophotometer connected to Shimadzu TCC-ZUOA temperature controller unit (Japan).

Infrared spectra
The infrared spectra were measured as KBr discs on Bruker-Tensor 37 Fourier transform infrared spectrophotometer (USA), evacuated to avoid water and CO_2 absorption.

^{1}H NMR spectra
The ^{1}H NMR spectra were obtained on a Bruker 600 MHz instrument using MS as an internal reference and d6-DMSO as the solvent.

Elemental analyses
C, H and N contents were determined with the Micro analyzer Perkin Elmer 2400 (USA).

Preparation of standard solutions of 2,3-DAP, CHA and DHBQ

Stock solutions of 2,3-DAP, CHA and DHBQ (5×10^{-3} mol L^{-1}) were freshly prepared before each series of measurements by dissolving precisely weighted amounts in the appropriate volume of EtOH. The stock solutions of donor and acceptor were protected from light. Solutions for spectroscopic measurements were made by mixing appropriate volumes of donor and acceptor stock solutions with the solvent.

Preparation of the solid 1:1 complexes 2,3-DAP-CHA and 2,3-DAP-DHBQ

The solid CT-complexes (1:1) between 2,3-DAP and CHA and between 2,3-DAP and DHBQ were prepared by mixing equimolar amounts of 2,3-DAP with CHA and 2,3-DAP with DHBQ in EtOH. The resulting complexes solutions were allowed to evaporate slowly at room temperature where the complexes were isolated as reddish purple and reddish-brown crystals for 2,3-DAP-CHA and 2,3-DAP-DHBQ complexes respectively. The separated complexes were filtered off, washed well with EtOH and dried over calcium chloride for 24 h.

Elemental analysis, as percentages, were determined for the (2,3-DAP-CHA) $C_{11}H_9N_3O_4Cl_2$ complex: C, 41.53%; H, 2.85%; N, 13.21%. Found: C, 41.11%; H, 2.81%; N, 13.14%. MP. 237–238 °C.

For the (2,3-DAP-DHBQ) $C_{11}H_{11}N_3O_4$ complex: C, 53.01%; H, 4.45%; N, 16.86%. Found: C, 53.12%; H, 4.50%; N, 16.77%. MP. 225–226 °C.

Determination of the formation constants of the CT-complexes (K_{CT})

For the purpose of UV–Vis spectral determination of the formation constants (K_{CT}), we applied the minimum–maximum absorbance method according to the following procedure. One milliliter (CT-Acceptor) of freshly prepared stock solution (5×10^{-3} mol L^{-1}) was transferred into a series of 10 ml calibrated flasks. To each of these were added different concentrations of the freshly stock donor solution (1×10^{-2} mol L^{-1}) and diluted to the mark with ethanol. The least concentration of the added amine led to the minimum absorbance of the complex (A_{min}). The concentration of the donor is increased gradually and the absorbance is recorded at the absorption band of the CT-complexes (A_{mix}) until we got the highest constant absorbance (A_{max}). The CT-formation constants (K_{CT}) were estimated as given by the following equation:

$$A_{max} = A_{mix} + \frac{A_{mix} - A_{min}}{K_{CT} \times C_{amine}} \tag{1}$$

where A_{max} is the maximum absorbance of the complex, A_{min} is the minimum absorbance of the complex, A_{mix} is the complexes absorbance values between A_{max} and A_{min} and C_{amine} is the concentration of the added amine in mol L^{-1}.

The set of equilibrium constants were averaged [27].

Results and discussion

Electronic spectra

Fig. 1 shows the electronic absorption spectra of 2,3-DAP, CHA, DHBQ and CT-complexes in ethanol. While none of the reactants spectra displays any measurable absorption in the region 450–600 nm, the resulting CT-complexes show strong absorption bands centered at 526.0 and 485.5 for 2,3-DAP-CHA and 2,3-DAP-DHBQ complexes, respectively. These absorptions are associated with the strong change in color observed upon mixing of the reactants (red for 2,3-DAP-CHA and violet for 2,3-DAP-DHBQ from colorless
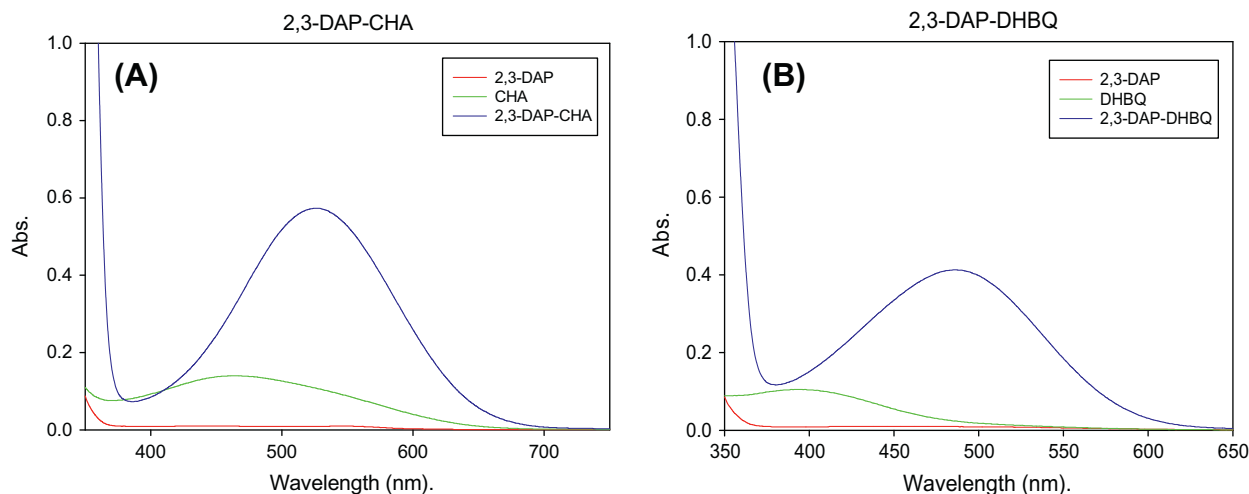
Fig. 1. Electronic spectra: (A) 5×10^{-4} M (2,3-DAP), 5×10^{-4} M (CHA) and $[5 \times 10^{-4}$ M (2,3-DAP) + 5×10^{-4} M (CHA)] (B) 2×10^{-4} M (2,3-DAP), 2×10^{-4} M (DHBQ) and $[5 \times 10^{-4}$ M (2,3-DAP) + 5×10^{-4} M (DHBQ)] in ethanol.

solutions in ethanol). These reflect the electronic transitions in the formed CT-complexes. It is important to report that the π-electronic spectra were scanned against the same electronic acceptors concentrations to eliminate the possible overlap that may arise between CT-complex and CHA or DHBQ bands. Moreover, it is worth mentioning that the formed new long wave length absorption bands are attributed to the formation of CHA and DHBQ radical anion resulting from complete transfer of charge from 2,3-DAP to CHA or DHBQ (Scheme 1). The radicals anion nature of benzoquinones has been confirmed by electron spin-resonance spectral measurements [35].

Effect of CHA and DHBQ concentrations on CT-complexes formation

Fig. 2 shows the effect of CHA and DHBQ concentration were studied by following the absorbance of the CT-complexes between varied amounts of 5×10^{-3} mol L^{-1} CHA and DHBQ with 1 mL of 5×10^{-3} mol L^{-1} 2,3-DAP in 10 mL calibrated flasks and diluted to the mark with solvent. It has been found that maximum constant absorbance of the CT-complexes were obtained with 1 mL of 5×10^{-3} mol L^{-1} CHA and DHBQ. The higher concentrations of CHA and DHBQ cause negligible increase in absorbance. On the

other hand, higher concentration of CHA and DHBQ may be useful to facilitate completion of the CT-complex that leads to minimize the required time for retaining the maximum absorbance at the corresponding wavelength.

Effect of reaction time on CT-complexes formation

The effect of time on the CT-reactions were studied by following the effect of time on the CT-complexes produced by mixing 5×10^{-4} mol L^{-1} from each of 2,3-DAP with CHA and DHBQ in ethanol. It have been found that the absorbance of the CT-complexes reached maximum and constant value instantly in the ethanol confirming that the time has no effect on the complexes absorbance. In addition, the formed CT-complex were stable for 2 h (Fig. 3).

Effect of temperature on CT-complexes formation

The effect of temperature was monitored by following the absorbance of the CT-complexes resulting by mixing 5×10^{-4} M CHA and DHBQ with different concentrations of 2,3-DAP at different temperatures (20–40 °C). It has been found that the formed CT-complexes were stable in the selected range at different 2,3-DAP
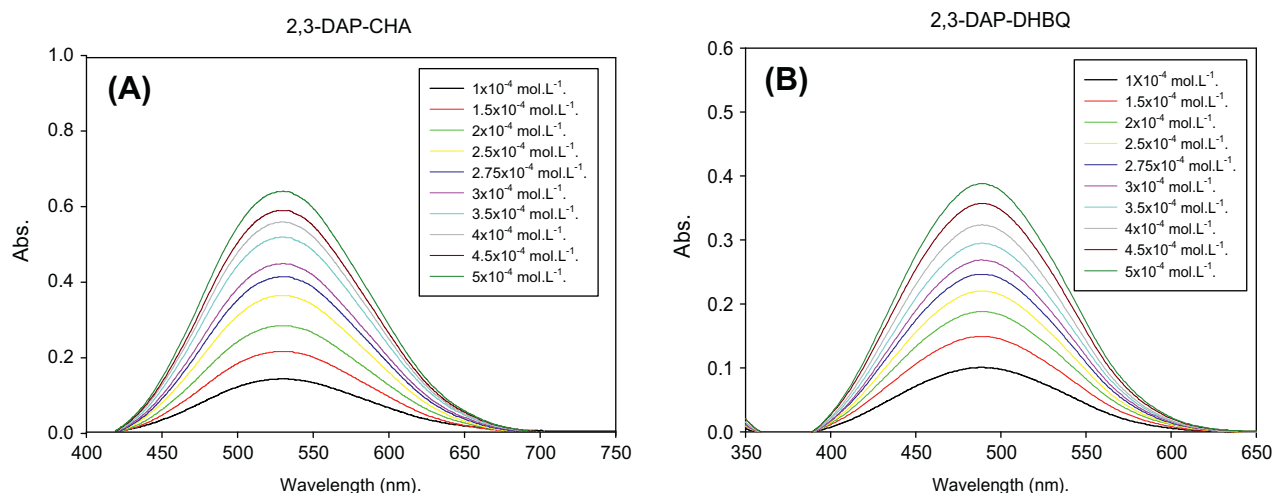

Fig. 2. Electronic spectra of 1:1 CT-complexes formation between 5×10^{-4} mol L^{-1} of (A) CHA and (B) DHBQ with various concentrations of 2,3-DAP in different solvents.
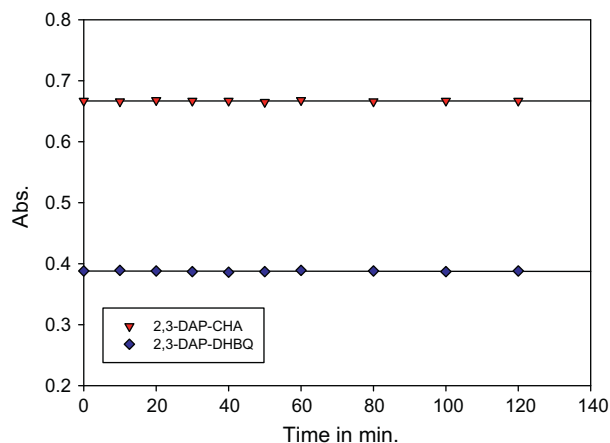
Fig. 3. Effect of time on the absorbance of 1:1 CT-complexes.

Table 1
Effect of 2,3-DAP concentrations on the absorbance of CT-complexes in methanol at different temperatures.

Conc. of 2.3,DAP (mol L^{-1})	20 °C	25 °C	30 °C	35 °C	40 °C
Absorbance of 2,3-DAP-CHA at λ_{max} = 526.0 nm					
1.00×10^{-4}	0.182	0.178	0.171	0.164	0.156
1.50×10^{-4}	0.206	0.199	0.182	0.177	0.168
2.00×10^{-4}	0.267	0.258	0.246	0.238	0.221
2.50×10^{-4}	0.352	0.338	0.316	0.288	0.274
2.75×10^{-4}	0.407	0.398	0.381	0.377	0.368
3.00×10^{-4}	0.438	0.426	0.419	0.406	0.395
3.50×10^{-4}	0.512	0.507	0.498	0.479	0.467
4.00×10^{-4}	0.561	0.547	0.521	0.518	0.509
4.50×10^{-4}	0.584	0.568	0.557	0.539	0.521
5.00×10^{-4}	0.642	0.631	0.629	0.607	0.595
Absorbance of 2,3-DAP-DHBQ at λ_{max} = 485.5 nm					
1.00×10^{-4}	0.096	0.085	0.078	0.064	0.052
1.50×10^{-4}	0.137	0.127	0.119	0.111	0.106
2.00×10^{-4}	0.188	0.175	0.168	0.154	0.146
2.50×10^{-4}	0.211	0.200	0.197	0.188	0.177
2.75×10^{-4}	0.229	0.215	0.206	0.199	0.178
3.00×10^{-4}	0.268	0.258	0.249	0.240	0.234
3.50×10^{-4}	0.294	0.288	0.279	0.265	0.255
4.00×10^{-4}	0.323	0.317	0.308	0.295	0.278
4.50×10^{-4}	0.357	0.344	0.335	0.317	0.308
5.00×10^{-4}	0.387	0.375	0.366	0.357	0.346

concentrations as can be understood from its constant absorbance at different temperatures (Table 1 and Fig. 4).

Stoichiometric ratio of the formed CT-complexes

The composition of the formed CT-complexes were determined by applying Job's method of continuous variations [36] and photometric titrations [37]. Fig. 5 represents the continuous variation plot where maximum absorbance were recorded at 0.5 mol fraction indicating 1:1 CT-complexes formation (2,3-DAP-CHA) and (2,3-DAP-DHBQ). Fig. 6 represents the photometric titrations where two straight lines were produced intercepting at 1:1 ratio (2,3-DAP-CHA) and (2,3-DAP-DHBQ). Accordingly, one can conclude from Figs. 5 and 6 that the CT-complexes are formed based on a 1:1 stoichiometric ratio (2,3-DAP-CHA) and (2,3-DAP-DHBQ).

Formation constants of the charge transfer reaction (K_{CT})

Based on the electronic spectra of the formed complexes at various concentrations of the donors, K_{CT} were estimated by using the minimum–maximum absorbances method, the results are
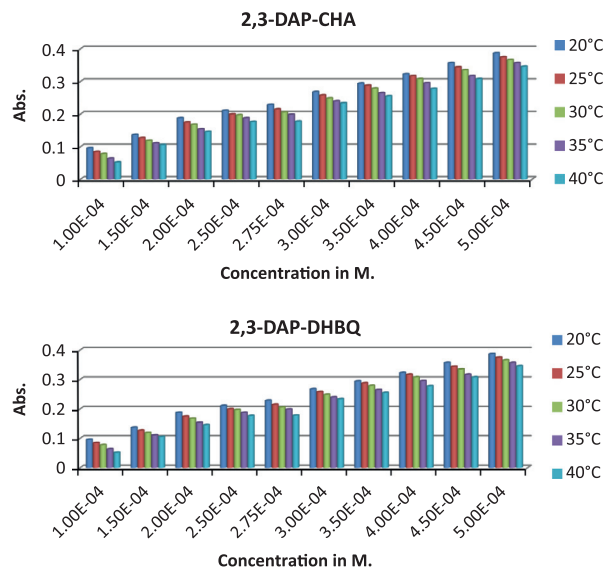

Fig. 4. Effect of temperature on the absorbance of CT-complexes at different concentrations of 2,3-DAP in ethanol.
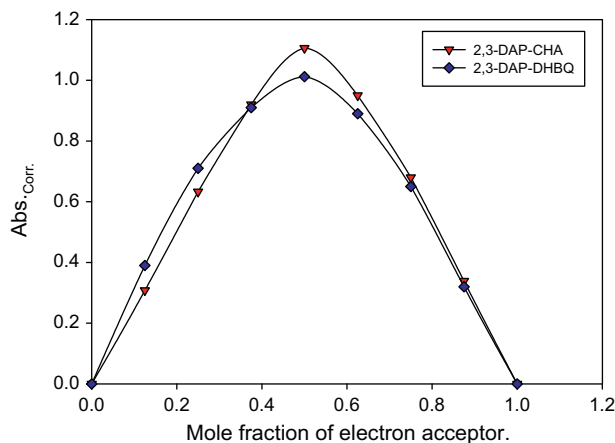

Fig. 5. Job's plots of CT-complexes in ethanol.

collected in Table 2. Generally, K_{CT} recorded higher values suggesting the formation of stable CT-complexes.

Calculation of the oscillator strength and the transition dipole moment

The oscillator strength (f) is a dimensionless quantity which used to express the transition probability of the CT-band [38] and the transition dipole moment (μ) of the CT-complexes [39]. The following expressions [40] are commonly used to calculate f and μ. The results are compiled in Table 3.

$$f = 4.32 \times 10^{-9}[\varepsilon_{max} \cdot \Delta v_{1/2}] \tag{2}$$

$$\mu = 0.0958[\varepsilon_{max} \cdot \Delta v_{1/2}/v_{max}] \tag{3}$$

where $\Delta v_{1/2}$ is the half band width of absorbance, ε_{max} and v_{max} are the molar extinction coefficient and wave number at the maximum absorption of the complex, respectively.

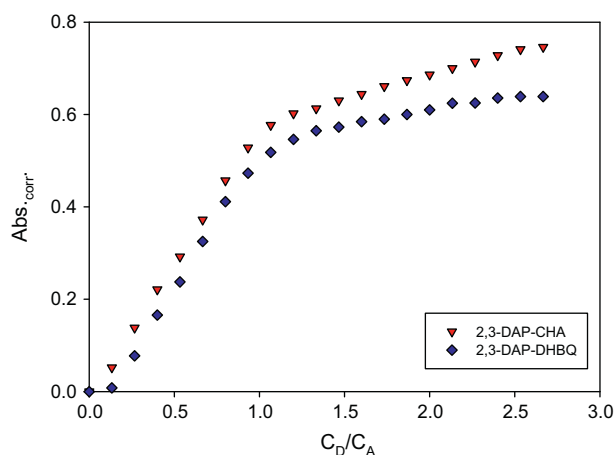**Fig. 6.** Photometric titration plots of CT-complexes in ethanol.

Table 3
Energy, ionization potential, dissociation energy, oscillator strength, dipole moment and free energy of CT-complexes formation in ethanol.

Donor	E_{CT} (eV)	I_P (eV)	W (eV)	$\Delta G°$ (kJ mol^{-1})	$f \times 100$	μ (Debye)
CHA	2.36	7.31	3.85	2.1440	6.24	8.715
DHBQ	2.56	8.16	4.50	2.1562	4.49	5.221

where hv_{max} is the π–π* transition energy in electron volts eV, *a* and *b* are 5.11 and 0.701 [43], 4.39 and 0.857 [44] or 5.156 and 0.778 [45], respectively. E_{CT}, mean values of I_P, $\Delta G°$ and W are collected in Table 3.

It is evident from Table 3 that the formed CT-complexes are characterized by relatively high values of both the oscillator strength and transition dipole moment. This confirms the charge transfer from 2,3-DAP to CHA and to DHBQ to form the red colored free radical anion of CHA and violet colored free radical anion of DHBQ.

The calculated values of the dissociation energy (W) of the CT-complexes in the EtOH are high suggesting that the investigated complexes are reasonably strong and stable under the studied conditions with high resonance stabilizing energy [46].

Furthermore, the negative values of the free energy change ($\Delta G°$) listed in Table 3 suggest the simultaneous production of the formed CT-complexes. Generally, the values of $\Delta G°$ given in Table 3 become more negative as the value of K_{CT} increases. As the bond between the donor and acceptor becomes stronger and thus the components are subjected to more physical strain or loss freedom, the values of $\Delta G°$ become more negative.

Calculation of the standard free energy change and dissociation energy

The standard free energy change of complexation ($\Delta G°$) was calculated from the formation constant (K_{CT}) according to the following equation [41]:

$$\Delta G^o = -2.303 RT \log K_{CT} \qquad (4)$$

where $\Delta G°$ is the free energy change of the complex (kJ mol^{-1}), R the gas constant (8.314 J mol^{-1} K), T is the absolute temperature (273 + °C) and K_{CT} is the formation constant of the CT-complex at 25 °C.

The dissociation energy (W) of the formed CT-complexes were calculated from the corresponding CT energy (E_{CT}), ionization potential of the donor (IP) and electron affinity of the acceptor (E_A) using the relationship [42]:

$$E_{CT} = I_P - E_A - W \qquad (5)$$

The energy of the π–π* interaction (E_{CT}) is calculated using the following equation [38]:

$$E_{CT} = 1243.667 / \lambda_{CT} \, \text{nm} \qquad (6)$$

whereas λ_{CT} is the wavelength of the CT-band of the formed complex.

The ionization potential values of the donors are calculated by using the following equation:

$$I_P = a + b(hv_{max}) \qquad (7)$$

Application of the studied CT-reaction

Based on the formation of colored CT-complexes between 2,3-DAP with CHA and DHBQ in EtOH, we propose in this section a simple, rapid and accurate spectrophotometric method for determination of 2,3-DAP. Under the optimum reaction conditions Beer's plots at various 1:1 M ratios between 2,3-DAP with CHA and DHBQ were constructed (Fig. 7). The regression equation in EtOH was calculated by the least square method. In all cases Beer's law plots were linear with very small intercepts and slopes and good correlation coefficients in the general concentration range 1.09–76.39 μg mL^{-1} (Table 4). The limits of detection and quantification were calculated according to the IUPAC definition [47]. The calculated values were listed in Table 4. They recorded small values confirming high accuracy of the method. It has been found also that the values of the confidence intervals of intercept α, and slope

Table 2
Minimum–maximum absorbances data at room temperature of the 2,3-DAP-CHA and 2,3-DAP-DHBQ CT-complexes in ethanol.

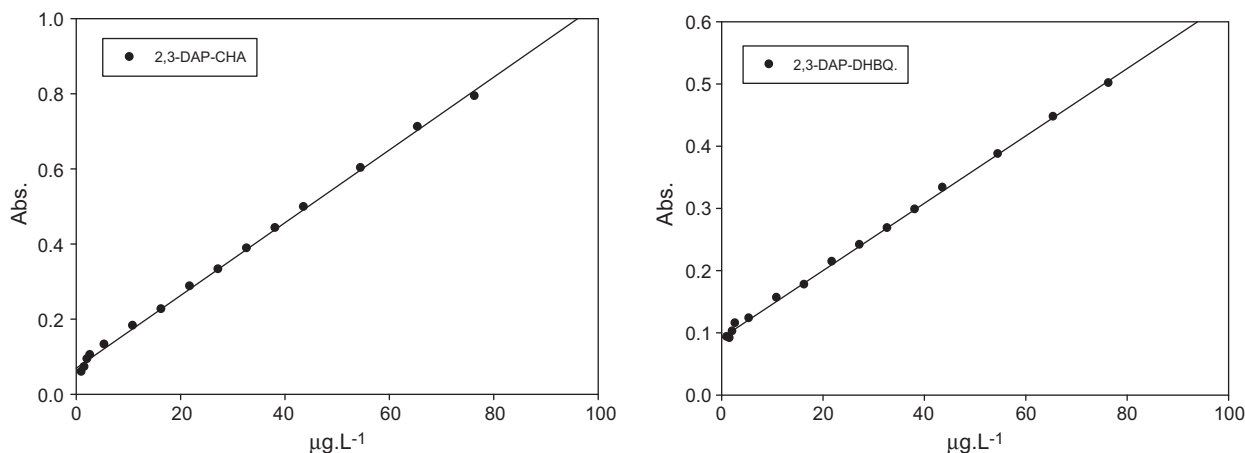| Complex	λ_{max} (nm)	$C_{2,3\text{-}DAP}$	A_{min}	A_{max}	$A_{complex}$	$K_{CT} \times 10^3$ (L mol^{-1})	Average $K_{CT} \times 10^3$ (L mol^{-1})
2,3-DAP-CHA	526.00	0.00015			0.206	366.9725	
		0.00020			0.267	1133.333	
		0.00025			0.352	2344.828	
		0.000275	0.182	0.642	0.407	3481.625	5732.793
		0.00030			0.438	4183.007	
		0.00035			0.512	7252.747	
		0.00040			0.561	11697.53	
		0.00045			0.584	15402.3	
2,3-DAP-DHBQ	485.50	0.00015			0.137	1093.333	
		0.00020			0.188	2311.558	
		0.00025			0.211	2613.636	
		0.000275	0.096	0.387	0.229	3060.99	6022.614
		0.00030			0.268	4817.927	
		0.00035			0.294	6082.949	
		0.00040			0.323	8867.188	
		0.00045			0.357	19333.33	

Fig. 7. Beer's law plot of CT complexes.

Table 4
Quantitative parameters of the [2,3DAP-CHA] and [2,3-DAP-DHBQ] CT complexes.

Parameter	CHA	DHBQ
Beer's law limits ($\mu g\,mL^{-1}$)	1.0913–76.3910	1.0913–76.3910
Limit of detection ($\mu g\,mL^{-1}$)	0.42502301	0.15449249
Limit of quantification ($\mu g\,mL^{-1}$)	1.416743	0.514975
Regression equation	$y = x9.688 \times 10^{-3} + 6.941 \times 10^{-2}$	$y = x5.411 \times 10^{-3} + 9.193 \times 10^{-2}$
Intercept, a	6.941×10^{-2}	9.193×10^{-2}
Slope, b	9.688×10^{-3}	5.411×10^{-3}
Confidence interval of intercept, α	$6.941 \times 10^{-2} \pm 3.816 \times 10^{-3}$	$9.193 \times 10^{-2} \pm 1.843 \times 10^{-3}$
Confidence interval of slope, β	$9.688 \times 10^{-3} \pm 1.067 \times 10^{-4}$	$5.411 \times 10^{-3} \pm 5.152 \times 10^{-5}$
Correlation coefficient, R^2	0.998	0.999

$Y = a + bx$, where y is the absorbance for concentration, x in $\mu g\,mL^{-1}$.

Table 5
Precision and accuracy of the method.

Complex	Amount taken $\mu g\,mL^{-1}$	Amount found $\mu g\,mL^{-1}$	Recovery %	$\overline{X}$	SD	RSD	$|\overline{X} - \mu|$	$\pm \frac{tS}{\sqrt{n}}$	Confidence limits
2,3-DAP-CHA	1.64	1.63	99.39						
	5.46	5.43	99.45						
	21.83	21.92	100.41	99.87	0.40	0.16	0.13	±0.42	99.87 ± 0.42
	38.20	38.27	100.18						
	65.48	65.41	99.89						
2,3-DAP-DHBQ	1.64	1.65	100.61						
	5.46	5.41	99.08						
	21.83	21.8	99.86	99.91	0.49	0.20	0.09	±0.52	100.40 ± 0.52
	38.20	38.19	99.97						
	65.48	65.49	100.02						

$t = 2.776$ for $n = 5$ at the 95% confidence level.
SD = standard deviation.
RSD = relative standard deviation.

β recorded small values confirming excellent linearity between the absorbance and concentration. The accuracy of the method was established by performing analysis of solutions containing five different amounts (within Beer's law limits) of 2,3-DAP and measuring the absorbance of their CT-complexes with CHA and DHBQ in EtOH. The concentration of 2,3-DAP was determined from the regression equation and then calculated the recovery percentages, the standard deviation (SD) and relative standard deviation (RSD). The recovery percentages were 99.87% and 99.91% with RSD 0.1643 and 0.2003 for 2,3-DAP-CHA and 2,3-DAP-DHBQ respectively, confirming high accuracy and precision of the proposed method (Table 5).

Comparison of the difference between the mean and true value $(\overline{X} - \mu)$ with the largest difference that could be expected as a result of indeterminate error $\left(\pm \frac{tS}{\sqrt{n}}\right)$ [48] has been carried out and the results were collected in Table 5. It has been found that $(\overline{X} - \mu)$ were less than $\left(\pm \frac{tS}{\sqrt{n}}\right)$ indicating that no significant difference between the mean and true value is existed.

Infrared spectra

Fig. 8 represents the infrared spectra of the donor (2,3-DAP), acceptors (CHA and DHBQ) and complexes (2,3-DAP-CHA and
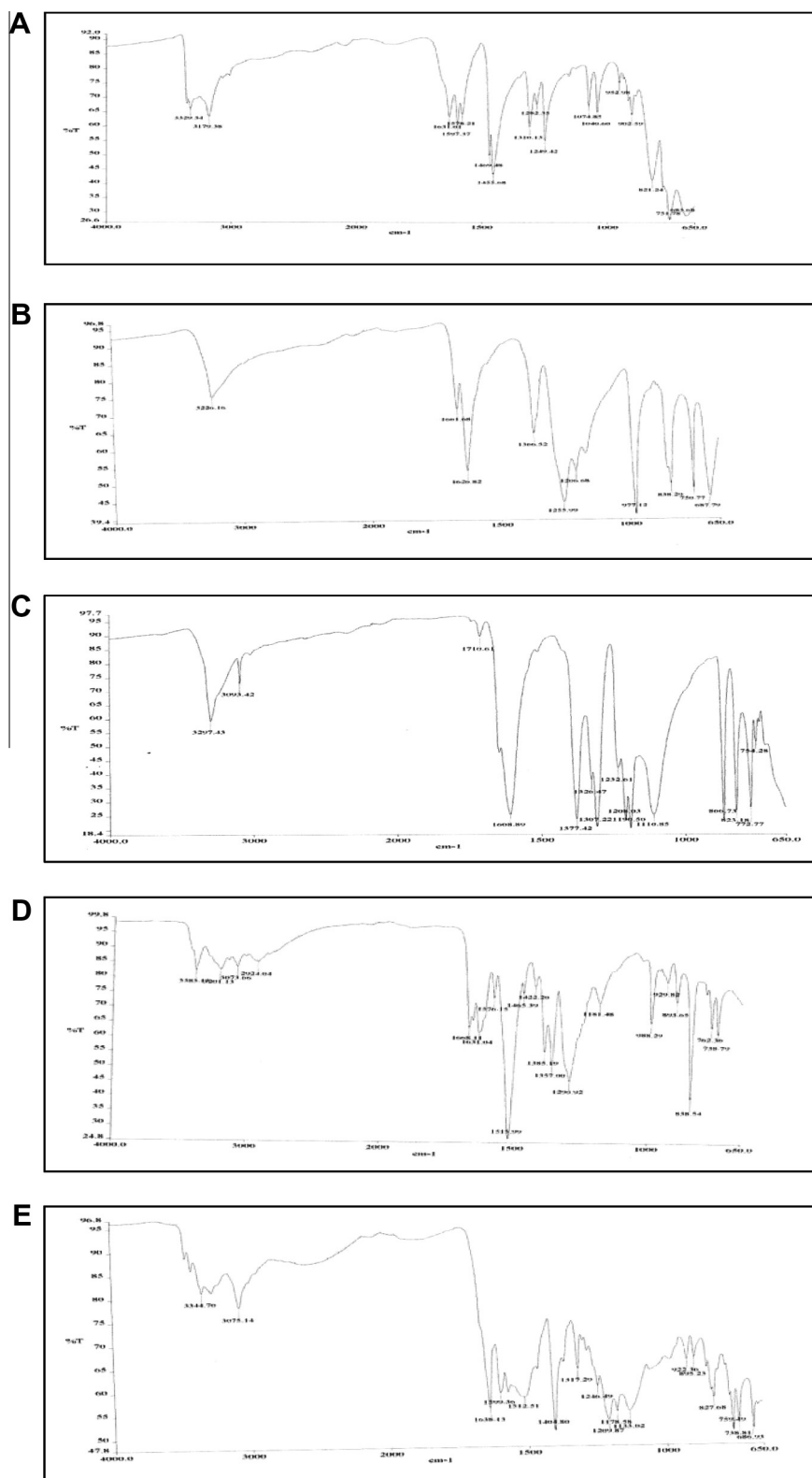
Fig. 8. FTIR spectra of (A) 2,3-DAP, (B) CHA, (C) DHBQ, (D) 2,3-DAP-CHA and (E) 2,3-DAP-DHBQ-CT complexes in the range 4000–650 cm^{-1}.

2,3-DAP-DHBQ). Main donor and acceptors vibrational frequencies are recognized in the presented complexes spectrum confirming the formation of a CT-complexes between 2.3-DAP and both CHA and DHBQ.

It is worth to mention that these frequencies are changed in intensity or frequency values a reset of the change in electronic structure upon complexation. For example the stretching vibrational frequencies v(C=C), v(C=N) and v(C—N) are recorded at 1570.15, 1515.99 and 1385.19 cm^{-1} and at 1599.30, 1512.61 and 1404.80 cm^{-1} in the complexes spectrum [(2,3-DAP-CHA) and (2,3-DAP-DHBQ)] compared with 1597.37, 1578.21 and 1455.08 cm^{-1} for 2,3-DAP alone.
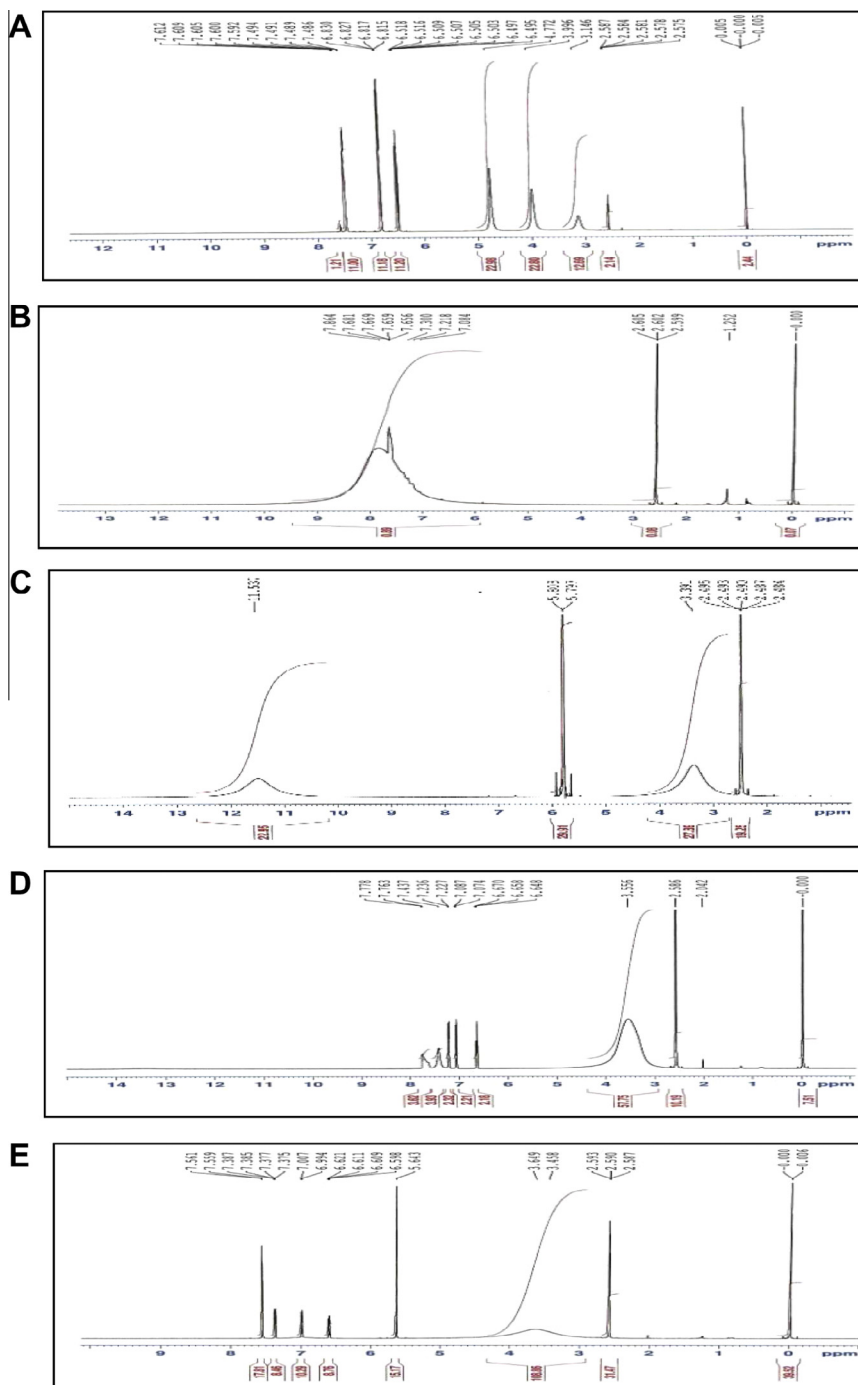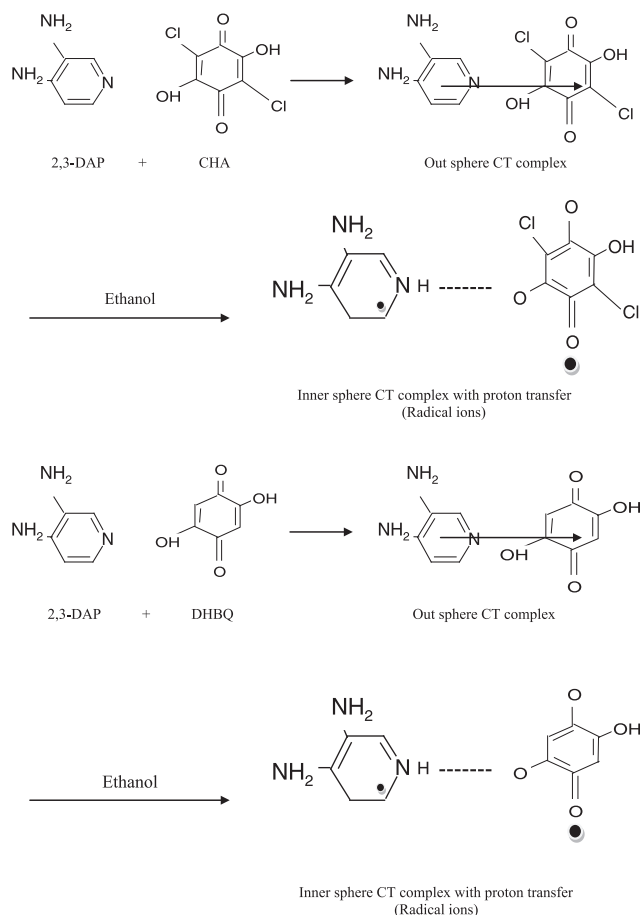
Fig. 9. ^{1}H NMR spectra of (A) 2,3-DAP,(B) CHA, (C) DHBQ (D) 2,3-DAP-CHA and (E) 2,3-DAP-DHBQ-CT complexes in d6-DMSO.

On the other hand and on comparing the acceptors spectrum CHA and DHBQ with the complexes one, it is clearly observed the blue shift of carbonyl group of the complexes to 1631.14 and 1638.13 cm^{-1} compared with 1608.89 and 1620.82 cm^{-1} for CHA and DHBQ alone, respectively.

Also, the in-plane bending vibrations of CHA and DHBQ are found at 1300.52, 1200.68 and 977.12 cm^{-1} for CHA and at 1307.22, 1208.08 and 1110.85 cm^{-1} for DHBQ compared with 1357.00, 1290.92 and 1181.48 cm^{-1} for 2,3-DAP-CHA complex and 1317.29, 1209.87, 1133.02 for 2,3-DAP-DHBQ complex.

Furthermore, the out of plane deformation of the carbonyl group δ(C=O) were recorded at 738.79 and 738.81 cm^{-1} in the complexes spectrum compared with 687.79 and 691.00 cm^{-1} for the acceptors alone.

In addition, the stretching vibration of the amine groups are appeared at 3179.38 cm^{-1} for 2,3-DAP compared with 3383.13 and 3073.66 cm^{-1} for the complexes [(2,3-DAP-CHA) and (2,3-DAP-DHBQ)], respectively. A very important finding from the complexes spectrum is the appearance of a weak broad band at 2924.04 cm^{-1} attributing to v(NH$^+$) and confirming the proton migration from

Scheme 2. Mechanism of the CT reaction.

Conclusion

1. 2,3-DAP reacts instantly with CHA and DHBQ to form CT-complexes in polar solvent (EtOH).
2. Job's method of continuous variation and photometric titration methods confirmed the formation of 1:1 CT-complex.
3. K_{CT} of CT-complexes in EtOH were estimated where K_{CT} recorded large value.
4. The solid CT-complexes were isolated and characterized using elemental analysis, IR and ^{1}H NMR.
5. The formed CT-complexes included proton transfer between OH of both CHA and DHBQ and the amino and ring nitrogen of 2,3-DAP.
6. Based on the simple composition of the formed CT-complexes and its instantaneous production, a rapid and accurate spectrophotometric method for analysis of 2,3-DAP was suggested.
7. Beer's law was obeyed in the concentration range 1.09–76.39 $\mu g\ ml^{-1}$.
8. The recovery percentages were 99.87% and 99.91% with relative standard deviation 0.16 and 0.20 for 2,3-DAP-CHA and 2,3-DAP-DHBQ respectively, confirming high accuracy and precision of the proposed method.

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the acceptors to the donor ring nitrogen. Hence, it is concluded that the infrared spectra is in full agreement with ^{1}H NMR is that the complexes include proton transfer beside charge transfer.

^{1}H NMR spectra

Fig. 9 represents the ^{1}H NMR spectrum of 1:1 [(2,3-DAP-CHA) and (2,3DAP-DHBQ)] CT-complexes in DMSO-d6. As can be seen in Fig. 9, two doublets are recorded at δ = 6.65 and δ = 7.78 ppm for 2,3-DAP-CHA and at δ = 6.59 and δ = 7.56 ppm for 2,3-DAP-DHBQ, respectively attributing to (C_3 and C_5) and (C_2 and C_8) protons of 2,3-DAP part of the complexes. These two doublets are down field shifted compared with 2,3-DAP alone whose doublets affirmed at δ = 6.51 and 7.49 ppm, respectively. This down field shift is expected due to the charge in electronic structure upon complexation. A sharp signal affirmed at 2.586 ppm for 2,3-DAP-CHA and at 2.590 for 2,3-DAP-DHBQ in Fig. 9 that could be assigned to the protons of the two amino groups of 2,3-DAP moiety. An important finding from Fig. 9 is the appearance of a new broad signal near δ = 3.65 ppm and is attributing to the proton on NH$^+$ group.–

Hence one can conclude the proton migration from OH of CHA and DHBQ towards the reach nitrogen of 2,3-DAP, the ring nitrogen. Hence, one concludes the existence of a proton transfer beside charge transfer in the formed complexes which is in concordance with the infrared results.

Based on the elemental analysis, infrared and ^{1}H NMR measurements, the mechanism of the studied reaction is deduced and shown in Scheme 2.

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