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ORIGINAL ARTICLE

# Charge-transfer interactions between piperidine as donor with different $\sigma$ - and $\pi$ -acceptors: Synthesis and spectroscopic characterization

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**Abstract** Charge-transfer (CT) complexes formed between piperidine (Pip) as donor with mono-iodobromide (IBr), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 2,6-dichloroquinone-4-chloroimide (DCQ), and 2,6-dibromoquinone-4-chloroimide (DBQ), as acceptors have been studied spectrophotometrically. The synthesis and characterization of piperidine CT-complexes of mono-iodobromide, [(Pip)(IBr)], 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, [(Pip)(DDQ)], 2,6-dichloroquinone-4-chloroimide, [(Pip)(DCQ)] and 2,6-dibromoquinone-4-chloroimide, [(Pip)(DBQ)] were described. These complexes are readily prepared from the reaction of Pip with IBr, DDQ, DCQ and DBQ within  $\text{CHCl}_3$  solvent. IR, UV–Vis techniques and elemental analyses (CHN), characterize the four piperidine charge-transfer complexes. Benesi–Hildebrand and its modification methods were applied to the determination of association constant ( $K$ ), molar extinction coefficient ( $\epsilon$ ).

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## 1. Introduction

The theory of charge-transfer interactions or the molecular complexes produced between electron donor and electron acceptor ownership Mulliken's (1950, 1952) this theory has been successfully applied to many interesting studies (Breigleb, 1961) amongst them is the possible role of CT-complexes in chemical reactions (Kosower, 1965). The charge-transfer (CT) interaction has been widely recently. Charge-transfer complexes are known to take part in many chemical reactions like addition, substitution and condensation (Fla et al., 1991; Roy et al.,

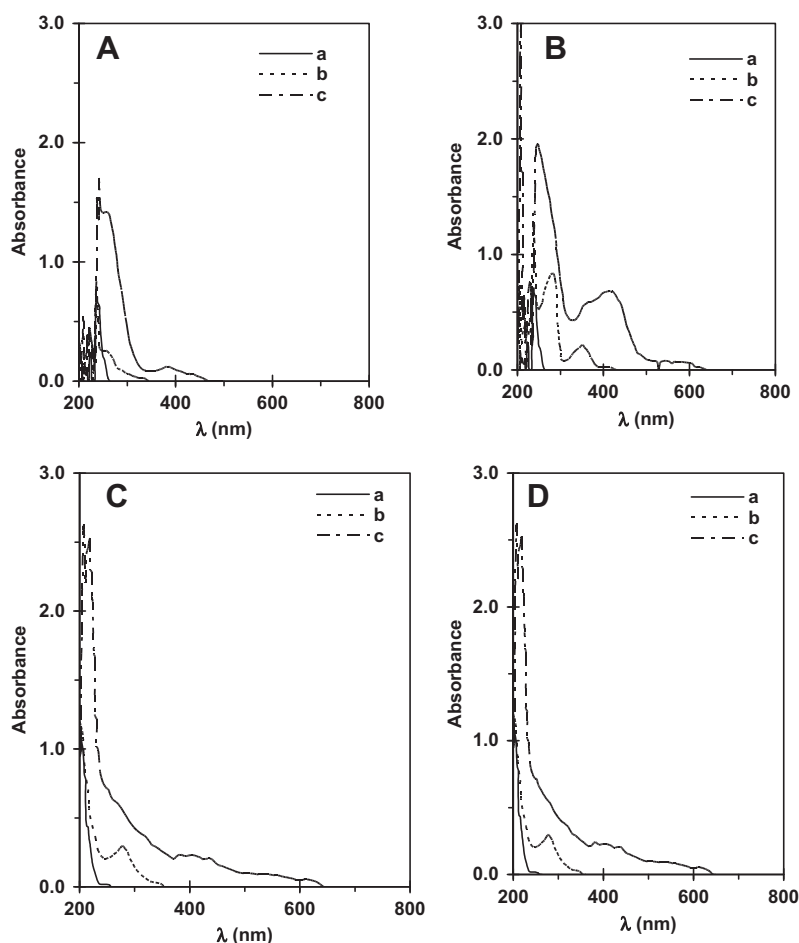
2000). These complexes have great attention for non-linear optical materials and electrical conductivities (Yakuphanoglu and Arslan, 2004a,b; Yakuphanoglu et al., 2005; Chakraborty et al., 2001). Electron donor–acceptor (EDA) interaction is also important in the field of drug-receptor binding mechanism (Korolkovas, 1998), in solar energy storage (Takahasi et al., 1993) and in surface chemistry (Andrade et al., 2000) as well as in many biological fields (Slifkin, 1971). On the other hand, the EDA reactions of certain  $\pi$ -acceptors have successfully utilized in pharmaceutical analysis (Abou Attia, 2000). For

these wide applications extensive studies on CT-complexes of  $\pi$ -acceptors have been performed (Basavaiah, 2004). In the literature survey (Fukunaga and Ishida, 2003; Abdel Sayed et al., 2003; Kandile and Latif, 1988; Muralikrishna et al., 1983) reveals that little attention has been paid to thermodynamic and electronic spectral characteristic does not contain any information on structure behavior of the CT interactions of this compound (Pip) with  $\sigma$ - and  $\pi$ -acceptors.

Charge-transfer complexes of organic species are intensively studied because of their special type of interaction,

**Table 1** Elemental analysis CHN and physical parameters data of the CT-complexes formed in the reaction of the Pip with IBr, DDQ, DCQ and DBQ.

Complexes (FW)	MW (g mol <sup>-1</sup> )	C (%)		H (%)		N (%)		Physical data	
		Found	Calc.	Found	Calc.	Found	Calc.	Color	mp (°C)
[(Pip)(IBr)] (C <sub>5</sub> H <sub>11</sub> NIBr)	291.96	20.45	20.55	3.66	3.76	4.56	4.79	Viscous brown	< 30
[(Pip)(DDQ)] (C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> Cl <sub>2</sub> O <sub>2</sub> )	312.16	49.25	49.97	3.54	3.52	13.41	13.45	Viscous brown	< 30
[(Pip)(DCQ)] (C <sub>11</sub> H <sub>13</sub> N <sub>2</sub> Cl <sub>3</sub> O)	295.60	44.39	44.65	4.23	4.39	9.44	9.47	Viscous brown	< 30
[(Pip)(DBQ)] (C <sub>11</sub> H <sub>13</sub> N <sub>2</sub> Br <sub>2</sub> ClO)	384.52	34.12	34.32	3.31	3.38	3.32	3.38	Viscous brown	< 30



**Figure 1** Electronic absorption spectra of: (A) Pip–IBr reaction in CHCl<sub>3</sub>, (B) Pip–DDQ reaction in CHCl<sub>3</sub>, (C) Pip–DCQ reaction in CH<sub>3</sub>OH and (D) Pip–DBQ reaction in CH<sub>3</sub>OH. (a) = donor ( $1.0 \times 10^{-4}$  M), (b) = acceptor ( $1.0 \times 10^{-4}$  M) and (c) = CT-complex.

which is accompanied by transfer of an electron from the donor to the acceptor (Das et al., 2000; Jones and Jimenez, 1999). Also, protonation of the donor from acidic acceptors are generally route for the formation of ion pair adducts (Smith et al., 1997, 1998, 2000).

## 2. Materials and methods

All chemicals used throughout this work were Analar or extra pure grade. Piperidine ( $C_5H_{11}N$ ), was of analytical reagent grade (Merck reagent). The acceptors were purchased from Aldrich. Stock solutions of piperidine or of acceptors were freshly prepared and the spectroscopic grade chloroform (Merck Co.) and methanol (BDH) were as used as received.

### 2.1. Preparation of piperidine-acceptor charge-transfer complexes (acceptor = IBr, DDQ, DCQ and DBQ)

#### 2.1.1. [Piperidine]-moniodobromide complexes

The solid CT-complex of (Pip) with IBr was prepared by mixing (85.15 mg, 1.0 mmol) of the donor in chloroform (10 ml), a solution of IBr was added (206.80 mg, 1.0 mmol) in the same solvent (10 ml) with continuously stirring for about 15 min at room temperature. A dark brown solid was isolated and the solution was allowed to evaporate slowly at room temperature. A viscous oily brown complex was formed, washed several times with little amounts of chloroform, and dried under vacuum over anhydrous calcium chloride; the empirical formula

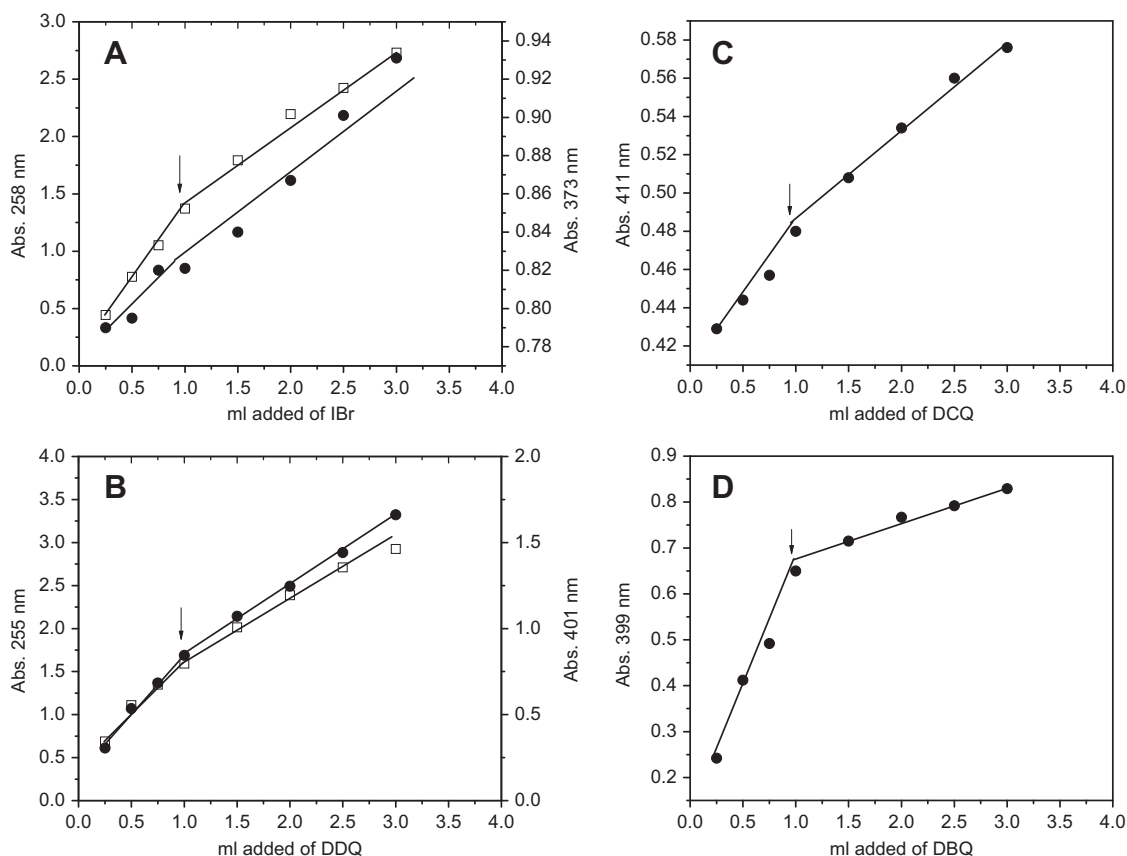
of the complex [(Pip)(IBr)], is  $C_5H_{11}NIBr$  with molecular weight 291.96 g/mol.

#### 2.1.2. [Piperidine]-DDQ, DCQ and DBQ complexes

The solid CT-complexes of (Pip) with acceptors (DDQ, DCQ and DBQ) were prepared by mixing 1 mmol of the donor in chloroform (10 ml) with 1 mmol of the each acceptors in the same solvent with constant stirring for about 15 min. The solutions were allowed to evaporate slowly at room temperature, the solids filtered and washed several times with little amounts of solvent, and dried under vacuum over anhydrous calcium chloride. The charge-transfer complexes [(Pip)(DDQ)] (viscous brown) formed with empirical formula as  $C_{13}H_{11}N_3Cl_2O_2$  with molecular weight 312.16 g/mol, [(Pip)(DCQ)] (viscous brown) formed with empirical formula as  $C_{11}H_{13}N_2Cl_3O$  with molecular weight 295.6 g/mol, [(Pip)(DBQ)] (viscous brown) formed with empirical formula as  $C_{11}H_{13}N_2Br_2OCl$  with molecular weight 384.52 g/mol.

### 2.2. Instrumentation and physical measurements

The electronic spectra of the donors, acceptors and the resulted CT-complexes were recorded in the region of (200–800 nm) by using a Jenway 6405 Spectrophotometer with quartz cells, 1.0 cm path in length. Photometric titration were performed at 25 °C for the reactions of donors with acceptors in chloroform, as follow: the concentration of the donors in the reaction mixtures was kept fixed at  $5.0 \times 10^{-4}$  M, while the



**Figure 2** Photometric titration curves for: (A) Pip-IBr system in  $CHCl_3$  at 258 and 373 nm, (B) Pip-DDQ system in  $CHCl_3$  at 255 and 401 nm, (C) Pip-DCQ system in  $CH_3OH$  at 411 nm and (D) Pip-DBQ system in  $CH_3OH$  at 399 nm.

concentration of acceptors were changed over a wide range from  $X \times 10^{-4}$  to  $Y \times 10^{-4}$  M. These produced solutions with donor: acceptor molar ratios varying from 1:0.25 to 1:4.00. IR measurements (KBr discs) of the solid donors, acceptor and CT-complexes were carried out on a Bruker FT-IR spectrophotometer ( $400\text{--}4000\text{ cm}^{-1}$ ).

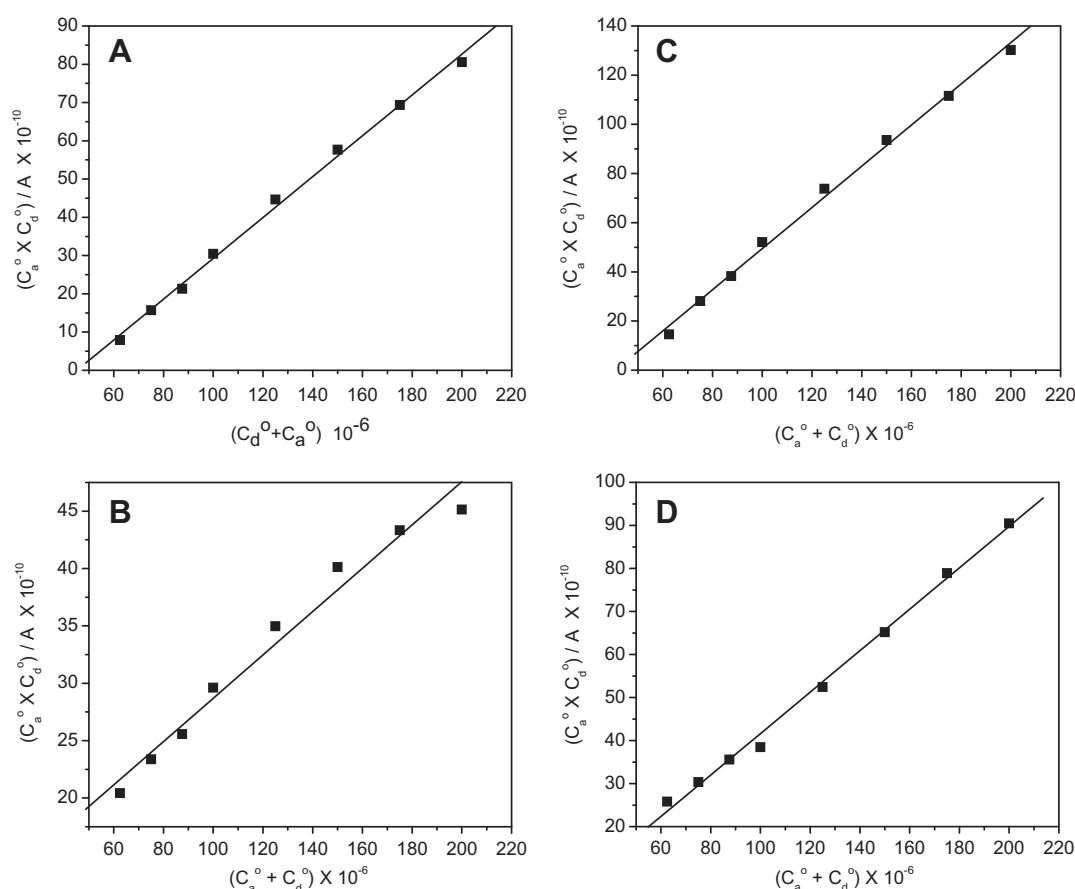
### 3. Results and discussion

Piperidine (Pip) represents an interesting class of simple aromatic compounds that participated in many organic reaction mechanisms. It is particularly important to study the CT interaction between Pip as an electron donor with mono iododibromide (IBr) as  $\sigma$ -acceptor and with some  $\pi$ -electron acceptors such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 2,6-dichloroquinone-4-chloroimide (DCQ) and 2,6-

dibromoquinone-4-chloroimide (DBQ). The elemental analysis (CHN), electronic spectra, photometric titration and mid infrared spectra were used to elucidate the nature of the interaction between donor and acceptor. The reactions of Pip with the IBr and  $\pi$ -acceptors were carried out in  $\text{CHCl}_3$  and/or  $\text{CH}_3\text{OH}$  as a solvent. The analytical data of the solid CT-complexes (C, H, and N contents) along with some of the physical behavior data are listed in Table 1.

#### 3.1. Electronic spectra of Pip/IBr, Pip/DDQ, Pip/DCQ and Pip/DBQ systems

The electronic spectra of the reaction mixtures containing IBr, DDQ, DCQ and DBQ with Pip as donor in  $\text{CHCl}_3$  and/or  $\text{CH}_3\text{OH}$  show absorption bands located at (258 and 373 nm) for Pip/IBr, at (255, 401 and 550 nm) for Pip/DDQ, at



**Figure 3** The plot of  $(C_d^0 + C_a^0)$  values against  $(C_d^0 \cdot C_a^0 / A)$  values for: (A) Pip-IBr system in  $\text{CHCl}_3$  at 373 nm, (B) Pip-DDQ system in  $\text{CHCl}_3$  at 401 nm, (C) Pip-DCQ system in  $\text{CH}_3\text{OH}$  at 411 nm and (D) Pip-DBQ system in  $\text{CH}_3\text{OH}$  at 399 nm.

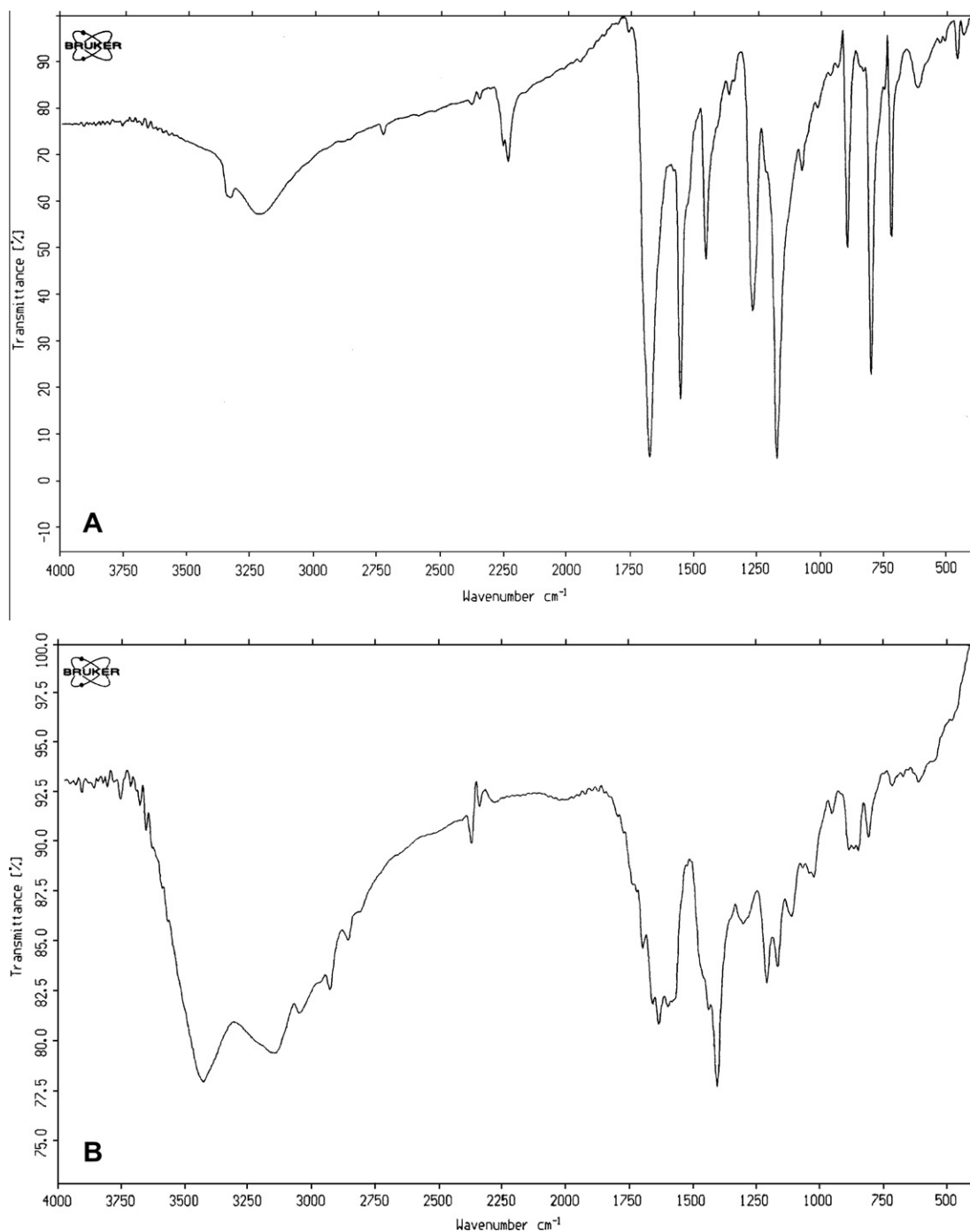
**Table 2** Spectrophotometric results of the CT-complexes of: (A) [(Pip)(IBr)], (B) [(Pip)(DDQ)] (C) [(Pip)(DCQ)] and (D) [(Pip)(DBQ)] CT-complexes.

Complex	$\lambda_{\text{max}}$ (nm)	$E_{\text{CT}}$ (eV)	$K$ ( $\text{mol}^{-1}$ )	$\varepsilon$ ( $\text{mol}^{-1} \text{cm}^{-1}$ )	$f$	$\mu$	$I_p$ (eV)
A	373	3.33	$2.48 \times 10^4$	$2.01 \times 10^4$	10.90	29.30	7.44
B	401	3.10	$1.41 \times 10^4$	$5.93 \times 10^4$	24.60	45.80	9.55
C	411	3.03	$2.67 \times 10^4$	$1.25 \times 10^4$	6.14	23.10	7.23
D	399	3.12	$12.43 \times 10^4$	$0.45 \times 10^4$	2.03	13.10	7.30

411 nm for Pip/DCQ and 399 nm for Pip/DBQ (Fig. 1A–D). These definite absorption bands do not belong to any of the reactants and well known to be characteristic of the formation of new CT-complexes; [(Pip)(IBr)], [(Pip)(DDQ)], [(Pip)(DCQ)] and [(Pip)(DBQ)]. Photometric titrations between (Pip) and mentioned acceptors; (IBr and DDQ) in  $\text{CHCl}_3$ , (DCQ and DBQ) in  $\text{CH}_3\text{OH}$  based on the (258 and 373 nm) for Pip/IBr, (255 and 401 nm) for Pip/DDQ, (411 nm) for Pip/DCQ and (399 nm) for Pip/DBQ systems reveals that the stoichiometry of the reactions is 1:1

(Fig. 2A–D). This was concluded on the bases of the obtained elemental analysis data of the isolated solid CT-complexes as indicated in the Table 1, as well as from the complexes infrared spectra, which indicate the existence of the bands characteristic for both the Pip and the acceptors.

In the photometric titration measurements, the concentration of Pip was kept fixed at  $1.00 \times 10^{-4}$  M, while the concentration of the acceptors was varied over the range of  $0.25 \times 10^{-4}$ – $3.00 \times 10^{-4}$  M. The stoichiometry of the CT-complexes was determined by applying molar ratio method (Skoog,



**Figure 4** Infrared spectra of: (A) DDQ, (B) DCQ, (C) DBQ, (D) [(Pip)(IBr)], (E) [(Pip)(DDQ)], (F) [(Pip)(DCQ)] and (G) [(Pip)(DBQ)] complexes.

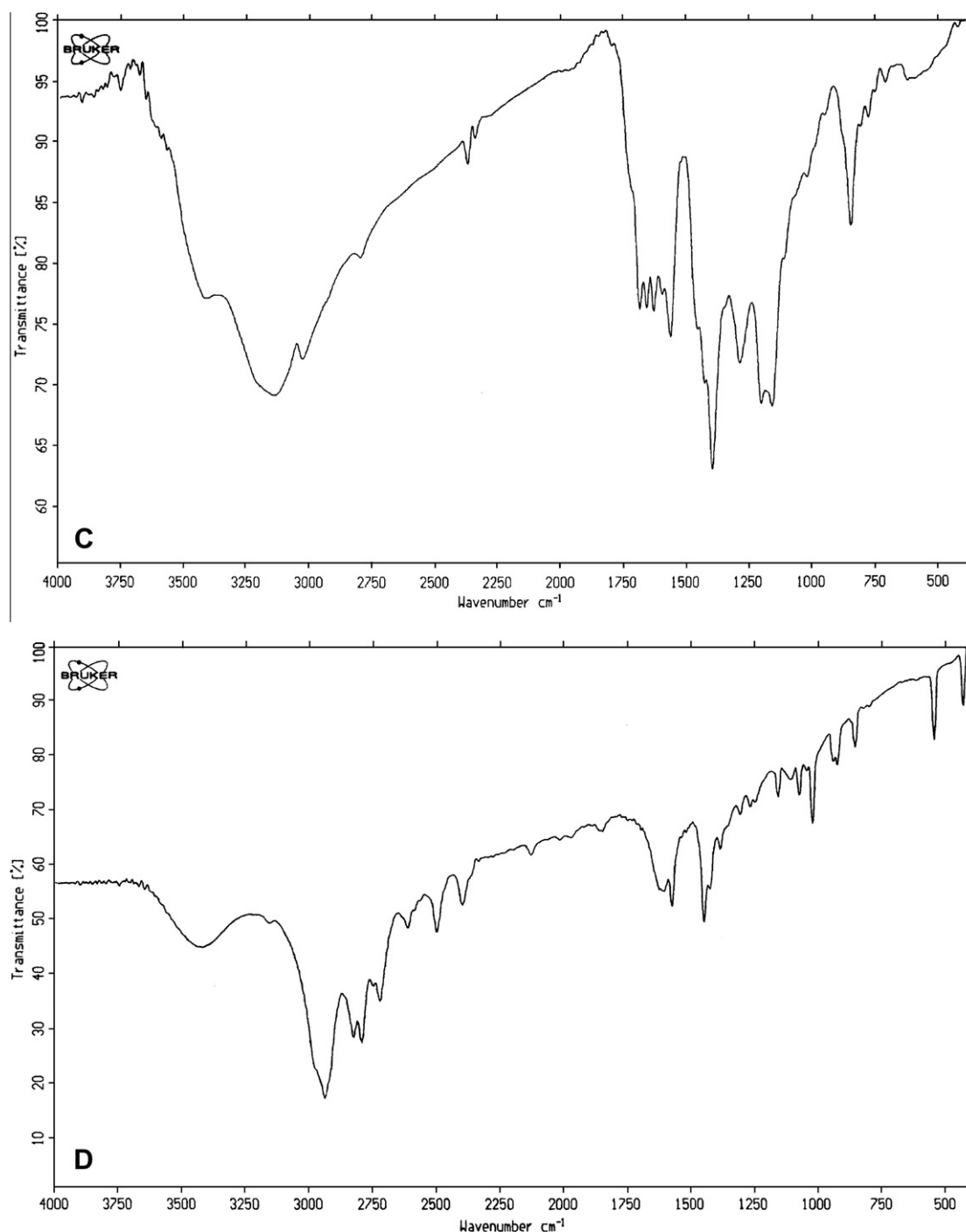


Fig. 4 (continued)

1985). The symmetric curves with maximum at 1.00 mol fraction indicate the formation of 1:1 CT-complexes (Fig. 2A–D). The association constant ( $K$ ) values and molar extinction coefficients ( $\epsilon$ ) of the CT-complexes studies have been determined using the 1:1 modified Benesi–Hildebrand Eq. (1) Abu-Eittah and Al-Sugeir, 1976.  $C_a^0$  and  $C_d^0$  are the initial concentrations of the represented acceptors (IBr, DDQ, DCQ and DBQ) and the donor Pip, respectively, while  $A$  is the absorbance of the CT-complexation bands around 258 and 373 nm for [(Pip)(IBr)], 255 and 401 nm for [(Pip)(DDQ)], 411 nm for

[(Pip)(DCQ)] and 399 nm for [(Pip)(DBQ)] complexes. Plotting the values of the  $(C_a^0 \cdot C_d^0 / A)$  against  $(C_a^0 + C_d^0)$  values for each acceptor, a straight lines are obtained with a slope of  $1/\epsilon$  and intercept of  $1/K\epsilon$  as shown in Fig. 3(A–D), for the reaction mixtures of Pip with (IBr and DDQ) and (DCQ and DBQ) in  $\text{CHCl}_3$  and  $\text{CH}_3\text{OH}$ , respectively. The values of both  $K$  and  $\epsilon$  associated with these complexes; [(Pip)(IBr)], [(Pip)(DDQ)], [(Pip)(DCQ)] and [(Pip)(DBQ)] are given in Table 2. The oscillator strength ( $f$ ) which is a dimensionless quantity used to express the transition probability of the CT band (Lever,

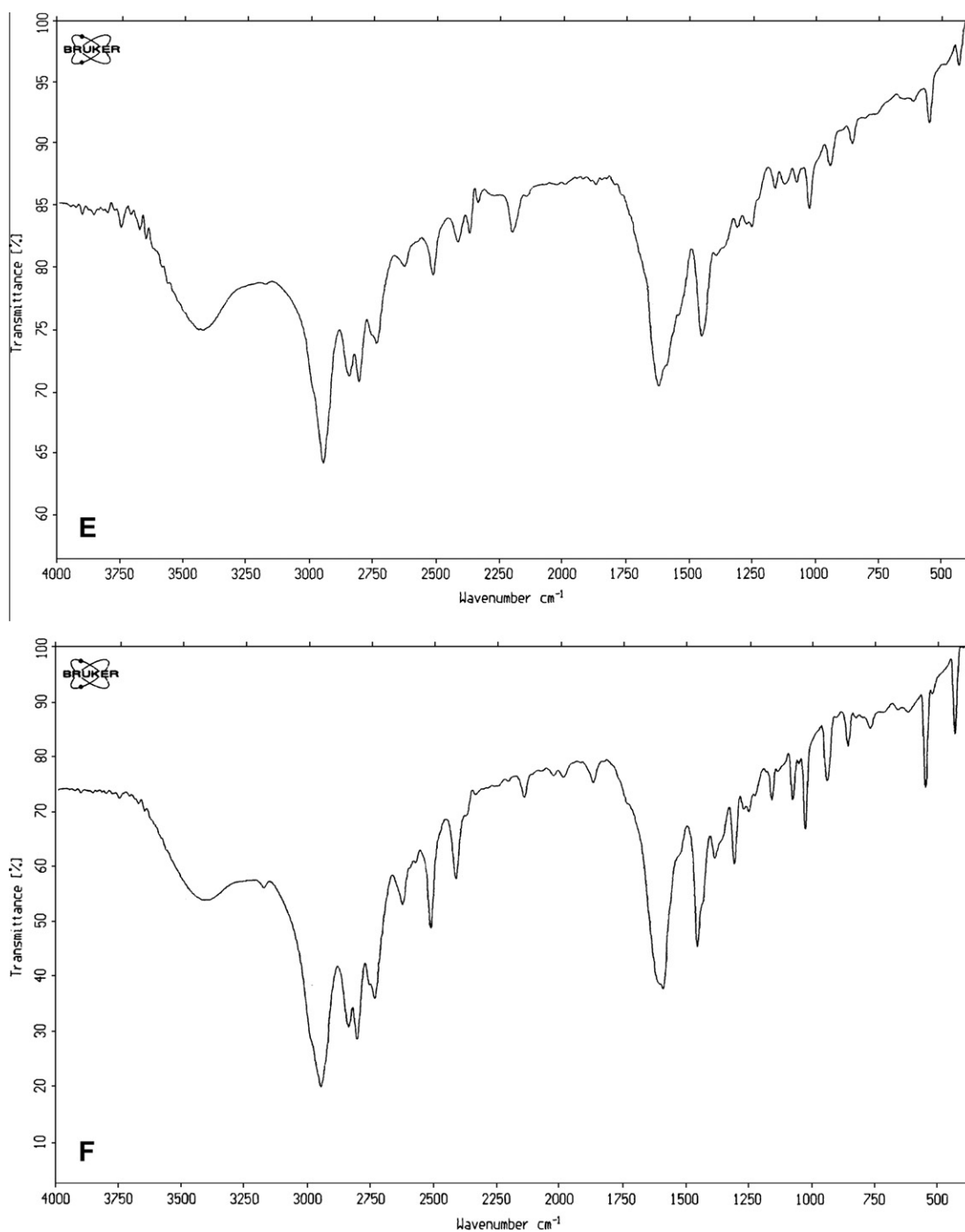


Fig. 4 (continued)

1985) and the transition dipole moment ( $\mu$ ) of the CT-complexes (Tsubomura and Lang, 1964). The high values of both the formation constant ( $K$ ) and the extinction coefficients ( $\epsilon$ ) of the resulted CT-complexes back to the expected high stabilities of the formed CT-complexes as a result of the expected high donation of the Pip nucleus.

This phenomena is also strongly supported by determined the dissociation energy ( $W$ ), which can be deduced from the corresponding CT energy, donor ionization potential ( $I_p$ ) and electron affinity of the acceptor (DDQ, 1.95 eV; CHL,

1.37 eV; CLA, 1.10 eV) by using the following Eq. (1) McConnell et al., 1964:

$$E_{CT} = I_p - E_A - W \quad (1)$$

The calculated value of ( $W$ ) in the case of DDQ as acceptor is 4.50 eV. The energy of the  $n-\pi^*$  interaction was calculated, where  $\lambda_{CT}$  is the wavelength of the CT band of the complexes; 3.33 eV (IBr), 3.10 eV (DDQ), 3.03 eV (DCQ) and 3.12 eV (DBQ).



The ionization potential ( $I_p$ ) of the free donor of the highest filled molecular orbital on the donor was determined from the CT energies of the CT band of its complexes with DDQ and CHL using the following Eqs. (2) and (3) Aloisi and Pignataro, 1973; Foster et al., 1969:

$$I_p \text{ (eV)} = 5.76 + 1.52 \times 10^{-4} \nu_{\text{DDQ}} \text{ (cm}^{-1}\text{)} \quad (2)$$

$$I_p \text{ (eV)} = 5.00 + 1.53 \times 10^{-4} \nu_{\text{CHL}} \text{ (cm}^{-1}\text{)} \quad (3)$$

where,  $\nu$  is the wavenumber corresponding to the CT band of the CT-complexes.

The equilibrium constants are strongly dependent on the nature of the used acceptor including the type of electron withdrawing substituents to it, such as cyano and halo groups. For example, Table 2, the value of equilibrium constant for [(Pip)(IBr)] and [(Pip)(DCQ)] complexes in  $\text{CHCl}_3$  and methanol, respectively, are almost the same. This value is about a twice times higher than the values of equilibrium constant for the complexes [(Pip)(DDQ)]. The [(Pip)(DBQ)] CT-complex has

a five times higher than IBr/Pip and DCQ/Pip complex and so higher by nine times comparison with [(Pip)(DDQ)] charge-transfer complex.

### 3.2. Infrared spectra

The Infrared spectra of the 1:1 CT-complexes formed from the interaction of the donor and the respected acceptors with the general formula, [(Pip)(acceptor)], together with the corresponding free acceptor (DDQ, DCQ and DBQ) and donor Pip, are shown in Fig. 4(A–G). Full assignments concerning the all of infrared bands were located in the spectra are listed in Table 3.

A comparison of the relevant IR spectral bands of the free donor, Pip and acceptors (DDQ, DCQ and DBQ) with the corresponding appeared in the IR spectra of the isolated solid CT-complexes clearly indicated that the characteristic bands of Pip show some shift in the frequencies (Table 3), as well as some change in their bands intensities. This could be attributed

**Table 3** Infrared frequencies<sup>a</sup> ( $\text{cm}^{-1}$ ) and tentative assignments for DDQ, DCQ, DBQ, [(Pip)(IBr)], [(Pip)(DDQ)], [(Pip)(DCQ)] and [(Pip)(DBQ)] complexes.

DDQ	DCQ	DBQ	[(Pip)(acceptor)] CT-complexes				Assignments <sup>b</sup>
			IBr	DDQ	DCQ	DBQ	
3325 w 3218 br	3424 s, br	3416 s, br	3426 s, br	3424 s, br	3401 s, br	3424 s, br	$\nu_{(\text{O}-\text{H})}$ ; $\text{H}_2\text{O}$ of KBr
–	3144 s, br 3047 mw 2927 mw 2855 mw	3139 s, br 3028 w	2948 vs 2834 w 2803 w 2731 w	2949 vs 2846 ms 2807 ms 2738 ms	3177 vw 2949 vs 2840 ms 2807 ms 2737 s	2949 vs 2841 s 2807 s 2737 ms	$\nu_{(\text{N}-\text{H})}$ $\nu_{\text{s}(\text{C}-\text{H})} + \nu_{\text{as}(\text{C}-\text{H})}$
–	–	–	2620 mw 2507 ms 2405 ms	2630 mw 2517 ms 2417 ms	2627 ms 2514 s 2416 s	2626 ms 2513 s 2414 ms	Hydrogen bonding
2250 vw 2231 ms	–	–	–	2201 ms	–	–	$\nu_{(\text{C}=\text{N})}$ ; DDQ
1673 vs	1696 w 1656 w 1634 mw	1686 w 1658 w 1631 w	–	1670 sh	–	1740 vw	$\nu_{(\text{C}=\text{O})} + \nu_{(\text{C}=\text{N})}$ ; DDQ, DCQ and DBQ
–	–	–	1615 ms	1623 vs	1619 vw	1620 mw	$\delta_{\text{def}(\text{N}-\text{H})}$ Ring breathing bands
1552 vs 1451 s	1598 w 1437 sh	1597 vw 1564 vs	1582 s 1456 s	1454 s	1593 vs 1457 vs	1584 ms 1457 s	$\nu_{(\text{C}=\text{C})}$ ; DDQ, DCQ and DBQ C–H deformation
1358 w 1267 s 1172 vs 1072 w	1403 vs 1300 s, br 1208 s 1165 ms 1112 mw 1024 ms	1398 vs 1290 s 1205 w 1161 w	1391 vw 1313 vw 1273 vw 1162 ms 1113 mw 1080 ms	1313 vw 1256 w 1163 w 1125 w 1079 w 1028 ms	1389 mw 1311 ms 1255 w 1162 ms 1080 ms 1030 s	1390 w 1313 w 1256 w 1163 ms 1079 w 1029 ms	$\nu_{(\text{C}-\text{C})} + \nu_{(\text{C}-\text{N})}$ CH, in-plane bend
1010 vw 893 s 800 vs 720 s	953 w 886 vw 849 vw 809 ms 715 w	848 s 778 vw 710 w	1028 s 929 ms 859 ms	947 859 mw	943 s 860 ms 773 w	941 ms 860 w 830 vw	$\delta_{\text{rock}}$ ; NH CH-deformation $\nu_{(\text{C}-\text{Cl})} + \nu_{(\text{C}-\text{Br})}$ ; DDQ, DCQ and DBQ
615 ms 527 vw 457 ms 432 mw	611 w 451 vw 438 vw	622 br 422 vw	549 s 434 s	617 vw 553 ms 436 ms	622 vw 553 s 437 s	621 vw 552 s 436 ms	Skeletal vibration CH bend CH out of plane bend Skeletal vibration CNC def.

<sup>a</sup> s = Strong, w = weak, m = medium, sh = shoulder, v = very, br = broad.

<sup>b</sup>  $\nu$ , Stretching;  $\delta$ , bending.



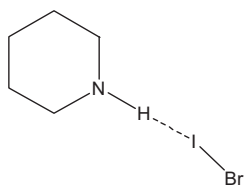
to the expected symmetry and electronic structure changes upon the formation of the CT-complex. The infrared explanation will take separately for each CT-complex to give an idea about the position of complexation as follows.

### 3.2.1. In the case of [(Pip)(IBr)] CT-complex

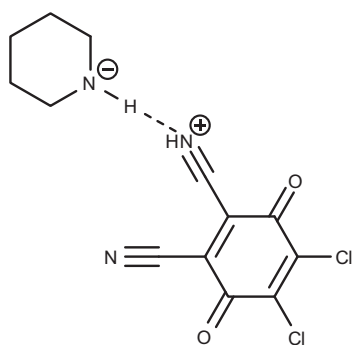
The vibration frequency of the  $\nu_{(N-H)}$  group for Pip observed at  $3393\text{ cm}^{-1}$  is shifted to  $3426\text{ cm}^{-1}$  in the IR spectrum of the CT-complex. The group of bands are exhibited at 2948, 2834, 2803 and  $2731\text{ cm}^{-1}$  in the [(Pip)(IBr)] complex assigned to  $\nu_{s(C-H)} + \nu_{as(C-H)}$  vibrations with small shift to lower wavenumbers compared with the free Pip. The spectrum of mono iodobromide/Pip complex includes a few medium strong absorption bands lying at 2620, 2507 and  $2405\text{ cm}^{-1}$  and could be assigned to hydrogen bonding (Bellamy, 1975). Importantly, in the spectrum of [(Pip)(IBr)] complex, the vibrations group of  $\delta_{(N-H)}$ ,  $\nu_{(C-N)}$ , CNC deformation show clearly changes compared with those of free Pip, Table 3. This observation proved that the complexation of (Pip) with IBr takes place via the  $-NH$  group through forming the hydrogen bonding as shown in Scheme 1.

### 3.2.2. In the case of [(Pip)(DDQ)] CT-complex

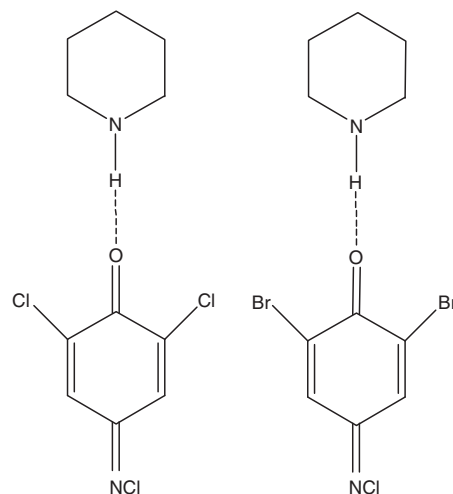
The IR spectra of the molecular complex of DDQ with Pip indicate the  $\nu_{(C\equiv N)}$  and  $\nu_{(C-Cl)}$  of the free acceptor are shifted to lower wavenumber values on complexation. Since DDQ is deprived from any acidic centers, thus we may conclude that the molecular complexes are formed through  $\pi-\pi^*$  and/or  $n-\pi^*$  charge migration from HOMO of the donor to the LUMO of the acceptor. Also, the shift of  $\nu_{(C=O)}$  of DDQ from higher to lower value on complex formation. IR spectrum of the molecular complex of DDQ with Pip indicate that the single  $\nu_{(C\equiv N)}$  of the free acceptor molecule which exhibited at ( $2250$  and  $2231\text{ cm}^{-1}$ ) was shifted to a lower wavenumber value ( $2201\text{ cm}^{-1}$ ) while the  $\nu_{(C=O)}$  absorption band of the free DDQ at  $1673\text{ cm}^{-1}$  was shifted to lower value



**Scheme 1** Structure of the [(Pip)(IBr)] CT-complex.



**Scheme 2** Structure of the [(Pip)(DDQ)] CT-complex.



**Scheme 3** Structure of the [(Pip)(DCQ)] and [(Pip)(DBQ)] CT-complexes.

( $1623\text{ cm}^{-1}$ ). Careful interpretation of IR spectra strongly supported that the CT interaction in the case of Pip/DDQ complex occurs through  $n-\pi^*$  transition deprotonation of  $-NH$  group of Pip to only one of the CN groups by forming intermolecular hydrogen bonding (Scheme 2). In addition, the characteristic bands of the hydrogen bonding are appearing in the IR spectrum of the studied complex at 2630, 2517, and  $2417\text{ cm}^{-1}$ , this group of bands are not existed in both spectra of the free donor and acceptor.

### 3.2.3. In the case of [(Pip)(DCQ)] and [(Pip)(DBQ)] CT-complexes

The IR spectra of the CT-complexes of DCQ and DBQ are characterized by a group of bands within the  $2338-2807\text{ cm}^{-1}$  range which are not present in the spectra of the free reactants. These bands are due to the stretching mode of a hydrogen bonding (Bellamy, 1975). This fact resulted from the hydrogen bond interaction through the proton ( $-NH$ ) of Piperidine donor and the oxygen atom of the carbonyl group of acceptor. This is further strongly supported by the clearly appearance of the peaks characteristic of the  $\nu_{(O-H)}$  at the wavelength 3401 and  $3424\text{ cm}^{-1}$  for DCQ and DBQ CT-complexes, respectively. The  $\nu_{(C=O)}$  group appearing at 1696, 1686, 1658, 1656 and  $1634\text{ cm}^{-1}$  are disappeared in the case of DCQ and shifted to  $1620\text{ cm}^{-1}$  for DBQ, this led us to predicted that the carbonyl group is involvement in the complexation. The shift of the infrared characteristic bands of the acceptor moiety to lower wavenumbers and the donor moiety to higher values reflects a donor to acceptor charge-transfer transition from  $\pi$  to  $\pi^*$  type, donor (HOMO)→acceptor (LOMO) Foster et al., 1969 (see Scheme 3).

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