Spectrochimica Acta Part A 79 (2011) 583–593

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

# *In situ* synthesis, photometric and spectroscopic studies of chelating system during the 1,4,7,10,13,16-hexaoxacyclooctadecane charge transfer reaction with different acceptors

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ARTICLE INFO

*Article history:*
Received 3 December 2010
Received in revised form 15 March 2011
Accepted 16 March 2011

*Keywords:*
Charge transfer complexes
p-CHL
DDQ
TCNQ
CLA
PA

ABSTRACT

Electron donor acceptor complexes (EDA) of the 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) as a rich donor were spectrophotometrically discussed and synthesized in solid form according the interactions with different nine of usual π-acceptors like 2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione (p-chloranil; p-CHL), tetrachloro-1,2-benzoquinone (o-chloranil; o-CHL), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetracyanoquinodimethane (TCNQ), 2,6-dichloroquinone-4-chloroimide (DCQ), 2,6-dibromoquinone-4-chloroimide (DBQ), 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid; CLA), *N*-bromosuccinimide (NBS), 2,4,6-trinitrophenol (picric acid; PA). Spectroscopic and physical data such as formation constant ($K_{CT}$), molar extinction coefficient ($\varepsilon_{CT}$), standard free energy ($\Delta G^\circ$), oscillator strength ($f$), transition dipole moment ($\mu$), resonance energy ($R_N$) and ionization potential ($I_p$) were estimated in chloroform or methanol at 25 °C. Based on the elemental analysis and photometric titrations the CT-complexes were formed indicated the formation of 1:1 charge-transfer complexes for the o-CHL, TCNQ, DCQ, DBQ and NBS acceptors but 1:3 ratio for p-CHL, DDQ, CLA and PA, respectively. The charge-transfer interactions were interpretative according to the formation of dative ion pairs [$18C6^{\bullet +}$, $A^{\bullet -}$], where A is acceptor. All of the resulting charge transfer complexes were isolated in amorphous form and the complexes formations on IR and $^1$H NMR spectra were discussed.

## 1. Introduction

18-Crown-6 is an organic compound with the formula $C_{12}H_{24}O_6$ and the IUPAC name of 1,4,7,10,13,16-hexaoxacyclooctadecane. Crown ethers coordinate with some metal cations in their central cavity. Crown ethers are useful as phase transfer catalysts [1,2]. Commonly, crown ethers have many interested properties such as the relative size of the ion and the hole of polyether [3] the number of O atoms [4] the basicity of O atoms [5] the steric hindrance in polyether ring [6] the tendency of the ion to associate with solvent. Macrocyclic polyethers like crown ether have received much attention in the last few years both in chemistry and biology [7]. These compounds act antiulcerogenically against histamine induced ulcers [8] and as antibacterial agents [9]. Crown ethers play an important role in non-biological activity (viz. in surfactant [10] and detergent [11] action and molecular semiconductivity [12]). There is significant interesting in the study of charge transfer complex of crown ethers with different π- and σ-acceptors [13–16]. The goal of this work is describing nine charge transfer complexes of 18-crown-6 as a donor with different types of acceptors (p-CHL, o-CHL, DDQ, TCNQ, DCQ, DBQ, CLA, NBS, PA) in CT interactions.

## 2. Experimental

### 2.1. Materials

18-Crown-6 (18C6, Aldrich) and π-acceptors from Merck Co. were used without any further purification. The structures of 18-crown-6 ether and the π-acceptors are shown in Formula I.

### 2.2. Synthesis of 18-crown-6 CT complexes

The solid CT complexes of 18-crown-6 with p-CHL, o-CHL, DDQ, TCNQ, DCQ, DBQ, CLA, NBS, and PA were prepared by mixing 1 mM

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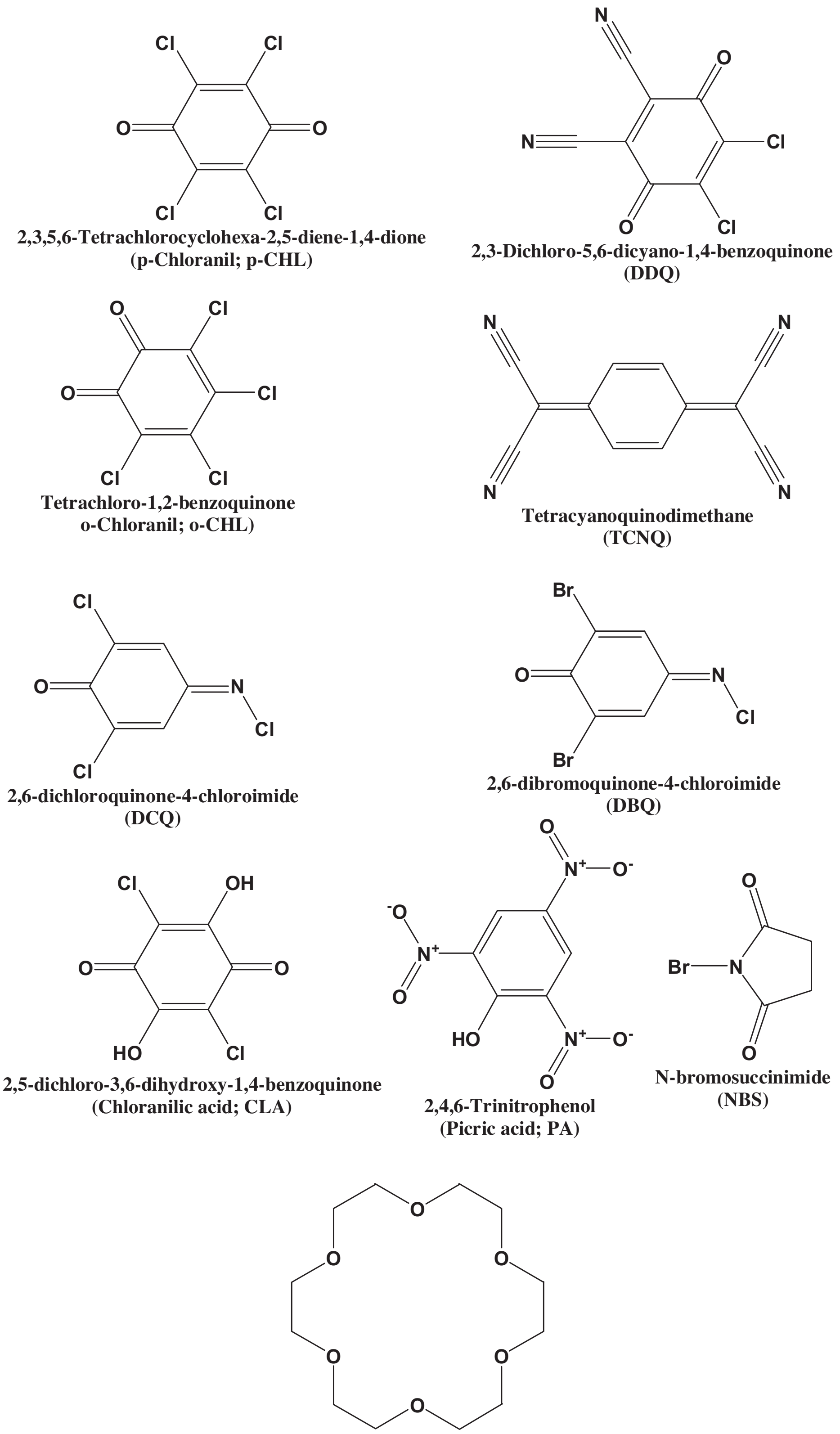
doi:10.1016/j.saa.2011.03.039



**Formula I.** Structure of 18-crown-6 and π-acceptors.

of the 18C6 as a donor in chloroform (30 mL) for all complexes except for (DCQ and DBQ in methanol) with 1 mM of each acceptor. The mixture was stirred at room temperature for 1 h, where solid complexes were obtained. The complexes were filtered off, washed with chloroform, and dried under vacuum.

### *2.3. Measurements*

Jenway 6405 (Bibby Scientific Limited, Beacon Road, Stone, Staffordshire ST15 0SA, UK) with quartz cell with a 1.0 cm path length was used from 800 to 200 nm. A Genesis II FT IR spectrophotometer (Mattson Instruments, USA) was used to take the IR spectra of the reactants and the CT-complexes as KBr discs. $^1$H NMR spectra of 18C6/DDQ and 18C6/TCNQ complexes were obtained on a Varian spectrophotometer Gemini 200 MHz (Agilent Technologies, Inc., USA) using TMS as internal reference and chloroform as the solvent. The elemental analyses of carbon, hydrogen and nitrogen contents were performed by the microanalysis unit at Cairo University, Egypt, using a Perkin Elmer CHN 2400 (USA).

### *2.4. Analytical data*

1 [(18C6)(p-CHL)$_2$]; $C_{24}H_{24}Cl_8O_{10}$; yellow color; Mol. wt. = 755.88; Calcd: %C, 30.10; %H, 3.17, Found: %C, 29.87; %H, 3.13.
2 [(18C6)(o-CHL)]; $C_{18}H_{24}Cl_4O_8$; dark red color; Mol. wt. = 510; Calcd: %C, 42.35; %H, 4.70, Found: %C, 42.11; %H, 4.49.
3 [(18C6)(DDQ)$_2$]; $C_{28}H_{24}Cl_4N_4O_{10}$; orange color; Mol. wt. = 718.12; Calcd: %C, 46.79; %H, 3.34; %N, 7.80, Found: %C, 46.33; %H, 3.09; %N, 7.44.
4 [(18C6)(TCNQ)]; $C_{24}H_{28}N_4O_6$; dark green color; Mol. wt. = 468.32; Calcd: %C, 61.50; %H, 6.00; %N, 11.96, Found: %C, 61.21; %H, 5.91; %N, 11.87.
5 [(18C6)(DBQ)]; $C_{18}H_{26}Br_2ClNO_7$; dark brown color; Mol. wt. = 560.94; Calcd: %C, 38.51; %H, 4.63; %N, 2.49, Found: %C, 38.25; %H, 4.31; %N, 2.36.
6 [(18C6)(DCQ)]; $C_{18}H_{26}Cl_3NO_7$; dark brown color; Mol. wt. = 473.04; Calcd: %C, 45.66; %H, 5.50; %N, 2.96, Found: %C, 45.44; %H, 5.32; %N, 2.84.
7 [(18C6)(CLA)$_2$]; $C_{24}H_{28}Cl_4O_{14}$; red color; Mol. wt. = 679.98; Calcd: %C, 42.35; %H, 4.12, Found: %C, 42.12; %H, 3.97.
8 [(18C6)(NBS)]; $C_{16}H_{28}BrNO_8$; yellow-orange color; Mol. wt. = 441.10; Calcd: %C, 43.53; %H, 6.35; %N, 3.17, Found: %C, 43.40; %H, 6.28; %N, 2.98.
9 [(18C6)(PA)$_2$]; $C_{24}H_{30}N_6O_{20}$; yellow color; Mol. wt. = 722.32; Calcd: %C, 39.87; %H, 4.15; %N, 11.63, Found: %C, 39.52; %H, 3.99; %N, 11.55.

## 3. Results and discussion

The elemental analysis data (C, H, and N) of the resulted CT-complexes were matched with the molar ratio gained from spectrophotometric titrations. Spectrophotometric titrations at 292, 307, 286, 406, 295, 286, 308, 280 and 421 nm were performed for the reactions of 18-crown-6 with p-CHL, o-CHL, DDQ, TCNQ, DBQ, DCQ, CLA, NBS, and PA, respectively, using the Jenway 6405 spectrophotometer as follows: A 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50 or 4.00 mL aliquot of a standard solution ($5.0 \times 10^{-4}$ M) of the appropriate acceptor (p-CHL, o-CHL, DDQ, TCNQ, DBQ, DCQ, CLA, NBS, and PA) in chloroform was added to 1.00 mL of $5.0 \times 10^{-4}$ M 18-crown-6 also in chloroform or methanol. The total volume of the mixture was 5 mL. The concentration of 18-crown-6 ($C_d^o$) in the reaction mixture was thus fixed at $1.0 \times 10^{-4}$ M while the concentration of π-acceptors ($C_a^o$) varied from $0.25 \times 10^{-4}$ M to $4.00 \times 10^{-4}$ M. These concentrations produce donor:acceptor ratios from 4:1 to 1:4. The absorbance of each CT complexes was measured and plotted as a function with the ratio of ($C_d^o$):($C_d^o$) according to a known method [17]. Solid samples of the 1:1 or 1:2 CT complexes of 18-crown-6 were prepared by mixing chloroform or methanol solutions of 18-crown-6 (1.0 mM) and either (p-CHL, o-CHL, DDQ, TCNQ, DBQ, DCQ, CLA, NBS, and PA) acceptor. It was of interest to observe that the solvent has a pronounced effect on the spectral intensities of the formed charge transfer complexes. To study this solvent effect in a quantitative manner, it was necessary to calculate the values of the equilibrium constant, *K*, the molar absorptivity ε, and the oscillator strength, *f*, of the 18-crown-6 complexes in the respective solvent.

The 1:1 modified Benesi–Hildebrand equation [18] was used in the calculations of the 18-crown-6 with o-CHL, TCNQ, DBQ, DCQ, and NBS charge transfer complexes,

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

where $C_a^o$ and $C_d^o$ are the initial concentrations of the acceptor (o-CHL, TCNQ, DBQ, DCQ, and NBS) and the donor 18-crown-6, respectively, and *A* is the absorbance of the strong bands at 307 nm for o-CHL, 406 nm for TCNQ, 295 nm for DBQ, 286 nm for DCQ, and 280 nm for NBS, respectively. When the $C_a^o C_d^o/A$ values for each 1:1 charge transfer complex are plotted against the corresponding $C_a^o + C_b^o$ values. Straight lines are obtained with a slope of $1/\varepsilon$ and intercept of $1/K\varepsilon$.

The spectrophotometric titrations of the intermolecular charge transfer complexes formed from the reactions of 18-crown-6 with p-CHL, DDQ, CLA and PA acceptors refereed to formation of 1:2 CT complexes. The 1:2 Eq. (2) [19] was used in the calculations.

$$\frac{(C_a^o)^2 C_d^o}{A} = \frac{1}{K\varepsilon} + \frac{1}{\varepsilon} C_a^o (4C_d^o + C_a^o) \tag{2}$$

where $(C_a^o)^2$ and $C_d^o$ are the initial concentration of the π-acceptor (p-CHL, DDQ, CLA and PA) and donor (18-crown-6), respectively, and *A* is the absorbance of the detected CT-band. The data obtained $C_d^o$, $(C_a^o)^2$, $C_a^o(4C_d^o + C_a^o)$ and $((C_a^o)^2 C_d^o)/A$ in chloroform were calculated. By plotting $((C_a^o)^2 C_d^o)/A$ values vs. $C_a^o(4C_d^o + C_a^o)$, straight lines were obtained with a slope of $1/\varepsilon$ and an intercept of $1/K\varepsilon$.

The spectroscopic and physical data such as formation constant ($K_{CT}$), molar extinction coefficient ($\varepsilon_{CT}$), standard free energy ($\Delta G^\circ$), oscillator strength (*f*), transition dipole moment ($\mu$), resonance energy ($R_N$) and ionization potential ($I_p$) were estimated in chloroform or methanol at 25 °C, and the different acceptors were found to have a pronounced effect on the interaction of 18-crown-6 with. These calculations can be summarized as follows;

The oscillator strength *f* was obtained from the approximate formula [20].

$$f = (4.319 \times 10^{-9}) \varepsilon_{\max} \nu_{1/2} \tag{3}$$

where $\nu_{1/2}$ is the band-width for half-intensity in cm$^{-1}$ and $\varepsilon_{\max}$ is the maximum extinction coefficient of the CT-band. The oscillator strength values are given in Table 1. The data resulted reveals several items. (i) The 18-crown-6/A (where A = p-CHL, o-CHL, DDQ, TCNQ, DBQ, DCQ, CLA, NBS, and PA) systems show high values of both formation constant (*K*) and molar absorptivity (ε). This high value of (*K*) reflects the high stability of the 18-crown-6 CT-complexes as a result of the expected high rich donation of the 18-crown-6 which contains six oxygen atoms. (ii) The different values of the oscillator strength, *f*, increases with increasing in the dielectric constant (*D*) of the solvent. This result could be explained on the basis of competitive solvent interactions with the acceptors [21,22].

The transition dipole moment ($\mu$) of the 18-crown-6 CT-complexes, Table 1, have been calculated from Eq. (4) [23];

$$\mu(\text{Debye}) = 0.0958 \left[ \frac{\varepsilon_{\max} \nu_{1/2}}{\nu_{\max}} \right]^{1/2} \tag{4}$$

The transition dipole moment is useful for determining if transitions are allowed, that the transition from a bonding π orbital to an antibonding π* orbital is allowed because the integral defining the transition dipole moment is nonzero.

The ionization potential ($I_p$) of the 18-crown-6 donor in their charge transfer complexes were calculated using empirical equation derived by Aloisi and Pignataro Eq. (5) [24,25];

$$I_p(\text{ev}) = 5.76 + 1.53 \times 10^{-4} \nu_{CT} \tag{5}$$

**Table 1**
Spectrophotometric results of the 18-crown-6 CT-complexes (A) [(18C6)(p-CHL)$_2$], (B) [(18C6)(o-CHL)], (C) [(18C6)(DDQ)$_2$], (D) [(18C6)(TCNQ)], (E) [(18C6)(DBQ)], (F) [(18C6)(DCQ)], (G) [(18C6)(CLA)$_2$], (H) [(18C6)(NBS)] and (I) [(18C6)(PA)$_2$].

| Complex | $\lambda_{max}$ (nm) | $E_{CT}$ (eV) | $K$ (l mol$^{-1}$) | $\varepsilon_{max}$ (l mol$^{-1}$ cm$^{-1}$) | $f$ | $\mu$ | $I_p$ | $D$ | $R_N$ | $\Delta G^\circ$ (25 °C) kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| A | 292 | 4.26 | $8.48 \times 10^7$ | 70,102 | 60.55 | 61.30 | 11.00 | 4.81 | 0.926 | 45,238 |
| B | 307 | 4.05 | 14,334 | 10,661 | 6.14 | 20.01 | 10.74 | 4.81 | 0.378 | 23,716 |
| C | 286 | 4.35 | $4.7 \times 10^7$ | 46,694 | 40.33 | 49.51 | 11.11 | 4.81 | 0.845 | 38,083 |
| D | 406 | 3.06 | 10,430 | 23,753 | 11.40 | 31.36 | 9.53 | 4.81 | 0.454 | 22,928 |
| E | 295 | 4.22 | 7783 | 34,129 | 21.06 | 36.33 | 10.95 | 32.70 | 0.733 | 22,202 |
| F | 286 | 4.35 | 15,667 | 30,211 | 21.75 | 36.35 | 11.11 | 32.70 | 0.719 | 23,936 |
| G | 308 | 4.04 | $1.43 \times 10^8$ | 61,043 | 52.73 | 58.74 | 10.73 | 4.81 | 0.848 | 46,532 |
| H | 280 | 4.44 | 11,100 | 8064 | 8.71 | 22.76 | 11.22 | 4.81 | 0.340 | 23,082 |
| I | 421 | 2.95 | $4.2 \times 10^7$ | 12,464 | 6.73 | 24.54 | 9.39 | 4.81 | 0.305 | 43,494 |

where $\nu_{CT}$ is the wavenumber in cm$^{-1}$ corresponding to the CT band formed from the interaction between donor and acceptor. The electron donating power of a donor molecule is measured by its ionization potential which is the energy required to remove an electron from the highest occupied molecular orbital.

The energy of the charge-transfer complexes $E_{CT}$ of the 18-crown-6 complexes is calculated using Eq. (6) [23];

$$E_{CT} = (h\nu_{CT}) = \frac{1243.667}{\lambda_{CT}} (\text{nm}) \quad (6)$$

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

Determination of resonance energy ($R_N$) [26] theoretically derived from Eq. (7);

$$\varepsilon_{max} = \frac{7.7 \times 10^{-4}}{h\nu_{CT}/[R_N] - 3.5} \quad (7)$$

where $\varepsilon_{max}$ is the molar absorptivity of the CT-complexes at maximum CT band, $\nu_{CT}$ is the frequency of the CT peak and $R_N$ is the resonance energy of the complex in the ground state, which, obviously is a contributing factor to the stability constant of the complex (a ground state property). The values of $R_N$ for the 18-crown-6 charge transfer complexes under study have been given in Table 1.

The standard free energy changes of complexation ($\Delta G^\circ$) were calculated from the formation constants by the following Eq. (8) [27];

$$\Delta G^\circ = -2.303RT \quad \log \quad K_{CT} \quad (8)$$

where $\Delta G^\circ$ is the free energy change of the CT-complexes (kJ mol$^{-1}$), $R$ is the gas constant (8.314 J mol$^{-1}$ K), $T$ is the temperature in Kelvin degrees (273+ °C) and $K_{CT}$ is the formation constant of the complexes (l mol$^{-1}$) in different solvents at room temperature.

### 3.1. p-CHL

The absorption spectrum of $1 \times 10^{-4}$ M p-CHL in the presence of $1 \times 10^{-4}$ M equal concentration of 18-crown-6 is shown in Fig. 1A. As can be seen, in the formation situation of intermolecular charge transfer the band appears at 292 nm is hyperchromicity. Therefore, the observation of this band can be assigned to the formation of charge transfer complex between 18C6 and p-CHL. 18-crown-6 and p-CHL in this complex behave as n-donor and π-acceptor, respectively. In order to obtain the stoichiometry of the resulting complex, the molar ratio method [17] was performed. The photometric plot is shown in Fig. 2A. The plot clearly indicates the formation of a 1:2 (donor:acceptor) complex. From Fig. 3A, the formation constant ($K$) and molar absorptivity ($\varepsilon$) were calculated using the relationship (Eq. (2)) deduced from plotting $((C_a^o)^2 C_d^o)/A$ values vs. $C_a^o(4C_d^o + C_a^o)$ employed the slopes and intercepts of these plots.

The IR spectral data of 18-crown-6, p-CHL and [(18C6)(p-CHL)$_2$] complex are presented in Table 2. The stretching of both C=O; p-CHL and –COC– of 18-crown-6 show a drastic shift to lower frequencies and decreasing the intensities upon molecular charge transfer complexation. These shifts are resulted from the building of higher charge density on the carbonyl groups of the p-CHL acceptor in the complex formation. However, the methylene stretching of the ethoxy groups of 18-crown-6 observed at 2894, 2872 and 2823 cm$^{-1}$ region considerably affected by shifted and decreasing the intensities of bands upon complex formation. This is probably due to the contribution of the ethoxy groups in the interaction with p-CHL acceptors.

According to these observations, the following equations are suggested for the interaction of 18C6 and p-CHL with 1:2 molar ratios.

$$18C6 + \text{p-CHL} = 18C6^{\bullet+}\text{p-CHL}^{\bullet-}$$

$$18C6^{\bullet+}\text{p-CHL}^{\bullet-} + \text{p-CHL} \rightarrow 18C6^{\bullet+}2\text{p-CHL}^{\bullet-}$$

The conductivity data of 18-crown-6 in the presence of p-CHL was measured and recorded small increases. This increasing in conductance after complexation proved that the charge transfer complexes formed from the formation of dative ion pairs. The spectral features of the [(18C6$^{\bullet+}$)(p-CHL$^{\bullet-}$)$_2$] complex is wholly consistent with Mulliken's formulation of weak complexes in which the new UV–vis absorption relates to the electronic transition ($h\nu_{CT}$) corresponding to [28].

### 3.2. o-CHL

The formation of charge transfer complex of o-CHL and 18C6 ether (Fig. 1B) with 1:1 stoichiometry. Here, this paper studied the stoichiometry of complex o-CHL with 18C6 by the molar ratio method using both concentration of [o-CHL]/[18C6]

**Table 2**
Characteristic infrared frequencies (cm$^{-1}$) and tentative assignments of 18C6, p-CHL and [(18C6$^{\bullet+}$)(p-CHL$^{\bullet-}$)$_2$] CT complex.

| 18C6 | p-CHL | [(18C6$^{\bullet+}$)(p-CHL$^{\bullet-}$)$_2$] | Assignments$^{(b)}$ |
|---|---|---|---|
| 2894 | – | | |
| 2872 | | | ν(C–H) |
| 2823 | | | |
| – | 1680 | 1647 | ν(C=O) |
| 1636 | 1583 | – | ν(C=C) |
| 1601 | 1555 | | |
| | 1528 | | |
| 1471 | – | 1471 | δ(CH) deformation |
| 1469 | | | |
| 1454 | | | |
| 1432 | – | 1351 | |
| 1361 | | 1285 | |
| 1345 | | 1249 | |
| 1285 | | 1108 | |
| 1279 | | | ν(C–O) |
| 1248 | | | ν(C–N) |
| 1235 | | | |
| 1229 | | | |
| 1108 | | | |
| 1058 | | | |

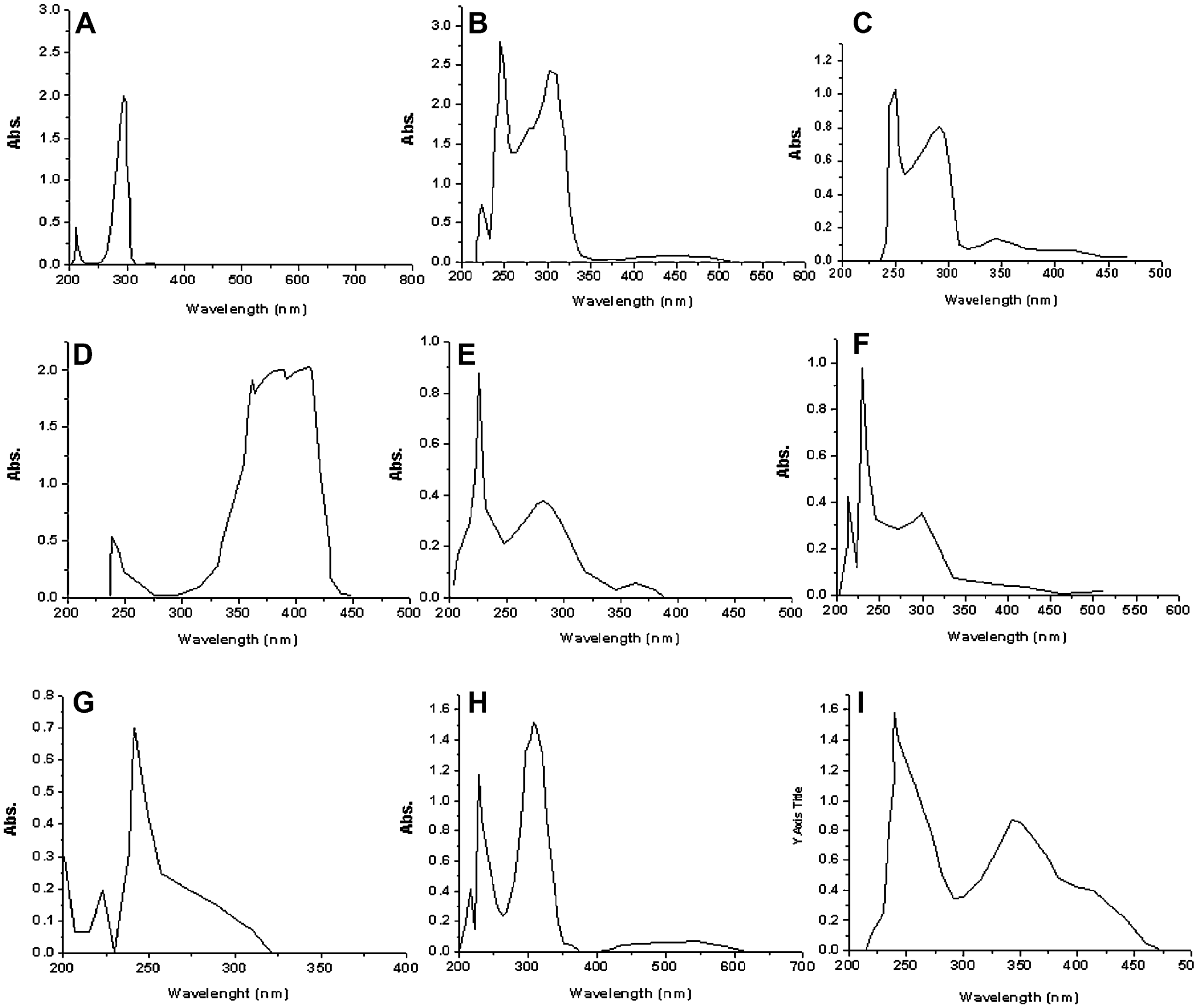


**Fig. 1.** Electronic spectrum of (A) 18C6/p-CHL, (B) 18C6/o-CHL, (C) 18C6/DDQ, (D) 18C6/TCNQ, (E) 18C6/DCQ, (F) 18C6/DBQ, (G) 18C6/NBS, (H) 18C6/CLA, and (I) 18C6/PA systems.

and absorbance measurements at $\lambda_{max} = 307$ nm. The resulting data of charge-transfer complex are shown in Fig. 2B. The Benesi–Hildebrand method [18] Eq. (1) was used for determination of both $\varepsilon$ and $K$ of the [(18C6)(o-CHL)] complex. The straight line plot of $C_a^o C_d^o / A$ vs. $C_d^o + C_d^o$ is shown in Fig. 4A. Consequently, the $\Delta G^\circ, f, \mu, R_N$ and $I_p$ values were estimated.

The characteristic bands in the infrared spectra of o-CHL, 18C6 and its CT-complex were selected and as signed in Table 3. The assignments data of [(o-CHL)(18C6)] complex show that the absorption band at 1680 cm$^{-1}$ which characteristic of the $\upsilon$(C=O) vibration of the carbonyl group in free o-CHL acceptor was blue shifted to 1646 cm$^{-1}$, that is indicative of the involvement of the C=O group in the charge transfer complexation.

**Table 3**
Characteristic infrared frequencies (cm$^{-1}$) and tentative assignments of o-CHL and [(18C6$^{\bullet+}$)(o-CHL$^{\bullet-}$)] CT complex.

| o-CHL | [(18C6$^{\bullet+}$)(o-CHL$^{\bullet-}$)] | Assignments$^{(b)}$ |
|---|---|---|
| – | | $\nu$(C–H) |
| 1682 | 1646 | $\nu$(C=O) |
| 1593 | – | |
| 1557 | | $\nu$(C=C) |
| 1514 | | |
| – | 1455 | $\delta$(CH) deformation |
| – | 1352 | |
| | 1286 | $\nu$(C–O) |
| | 1250 | $\nu$(C–N) |
| | 1108 | |

### 3.3. DDQ

Fig. 1C shows the absorption spectrum of 1.0 × 10$^{-4}$ M DDQ in the presence of 1.0 × 10$^{-4}$ M 18C6 gave the appearance of new band essentially at 286 nm. Fig. 2C shows the plots of absorbance vs. 18C6/DDQ mole ratio obtained at 286 nm. The plot show a break at 18C6/DDQ = 2 and further confirm the suggested mechanism;

$$18C6DDQ\ =\ 18C6^{\bullet+}DDQ^{\bullet-}$$

$$18C6^{\bullet+}DDQ^{\bullet-} + DDQ \rightarrow 18C6^{\bullet+}2DDQ^{\bullet-}$$

For evaluation of the equilibrium constant and the molar absorptivity of the resulting 1:2 18C6:DDQ complex (Eq. (2)) were calculated according to straight line (Fig. 3B) produced.

The IR spectral data of DDQ acceptor, the 1:2 charge transfer complex are presented in Table 4, as can be seen, the CN and CO stretching of DDQ show a drastic shift to lower (nearly absence)

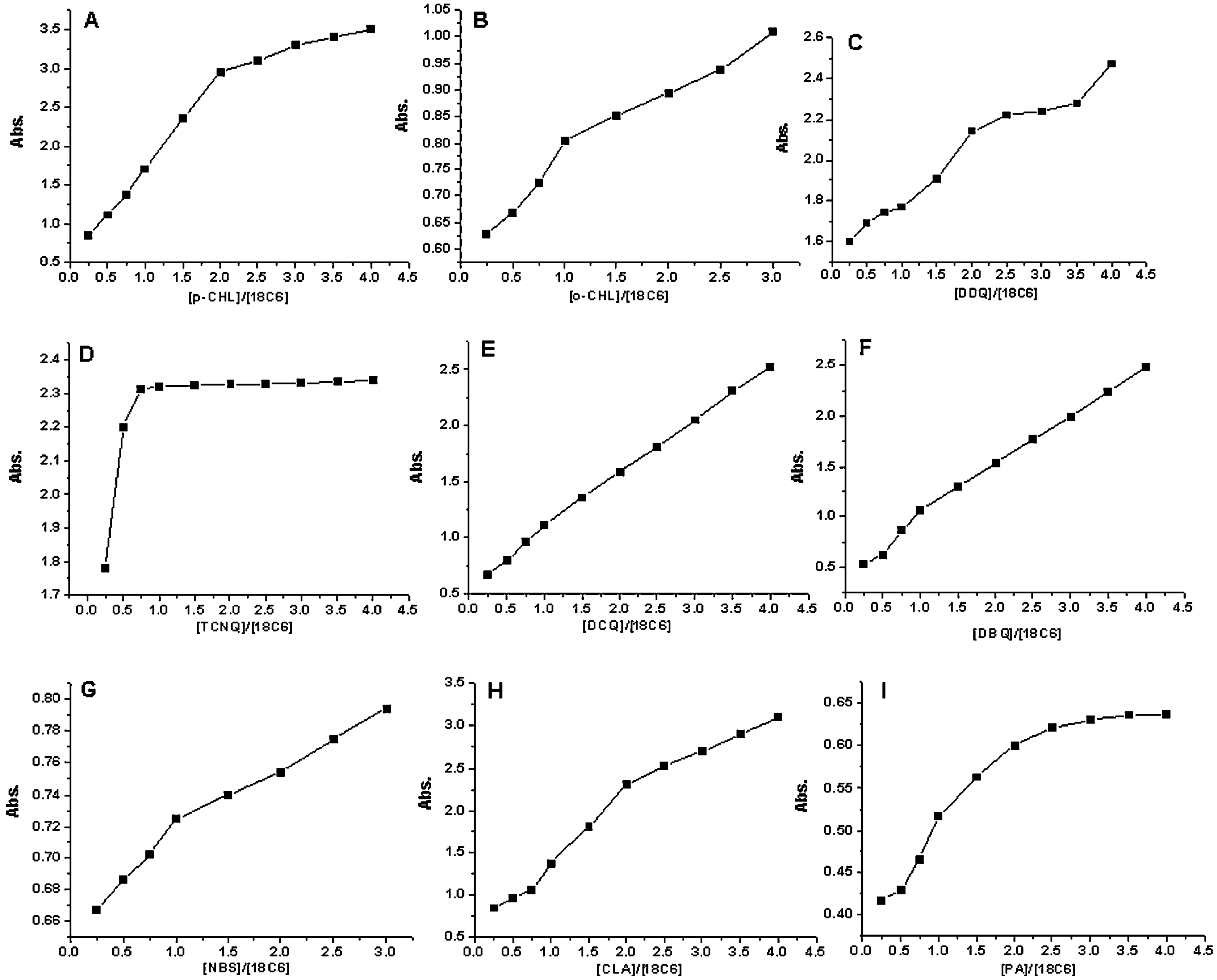


**Fig. 2.** Molar ratio curve of (A) 18C6/p-CHL, (B) 18C6/o-CHL, (C) 18C6/DDQ, (D) 18C6/TCNQ, (E) 18C6/DCQ, (F) 18C6/DBQ, (G) 18C6/NBS, (H) 18C6/CLA, and (I) 18C6/PA systems.

frequencies upon molecular complex formation with 18C6. These shifts are indicative of a higher charge density on the cyano and carbonyl groups of the DDQ acceptor of its transfer complex. However, the methylene stretching of the ethoxy groups of 18C6 observed within 2800 cm$^{-1}$ region was shifted upon the complex formation. This is probably due to the participation of the ethoxy groups in the interaction with DDQ acceptors.

**Table 4**
Characteristic infrared frequencies (cm$^{-1}$) and tentative assignments of DDQ and [(18C6$^{\bullet+}$)(DDQ$^{\bullet-}$)$_2$] CT complex.

| DDQ | [(18C6$^{\bullet+}$)(DDQ$^{\bullet-}$)$_2$] | Assignments$^{(b)}$ |
|---|---|---|
| – | 2891 | $\nu$(C–H) |
| | 2785 | |
| 2250 | 2070 | $\nu$(CN) |
| 2236 | | |
| 1680 | 1636 | $\nu$(C=O) |
| 1555 | 1474 | $\nu$(C=C) |
| 1430 | | |
| – | 1455 | $\delta$(CH) deformation |
| – | 1353 | $\nu$(C–O) |
| | 1286 | $\nu$(C–N) |
| | 1251 | |
| | 1105 | |

The $^1$H NMR spectrum of the 18-crown-6 CT complex was measured in CDCl$_3$ (Fig. 5). The spectrum of CT complex was compared with the free donor, which was found that only one signal was detected at 3.7 ppm due to protons of 12CH$_2$ of the aliphatic crown ether, this signal blue shifted indicating the involvement of the CH$_2$–O–CH$_2$ groups in complexation.

### 3.4. TCNQ

Fig. 1D shows the absorption spectrum of 1.0 × 10$^{-4}$ M TCNQ in the absence of 1.0 × 10$^{-4}$ M 18C6. As can be seen, over the range of 300–600 nm the intensity of TCNQ band at 406 nm within the [(18C6)(TCNQ)] complex increases comparison with the free TCNQ acceptor. Such observation is indicative of the formation of charge transfer complex through an equilibrium reaction. The formation of TCNQ$^{\bullet-}$ and 18C6$^{\bullet+}$ radical anions have been recorded frequently [29–31]. Based on these observations it can be concluded that the molar ratio between 18C6:TCNQ is 1:12 (Fig. 2D). To make check for the stability and reactivity of the TCNQ charge transfer com-

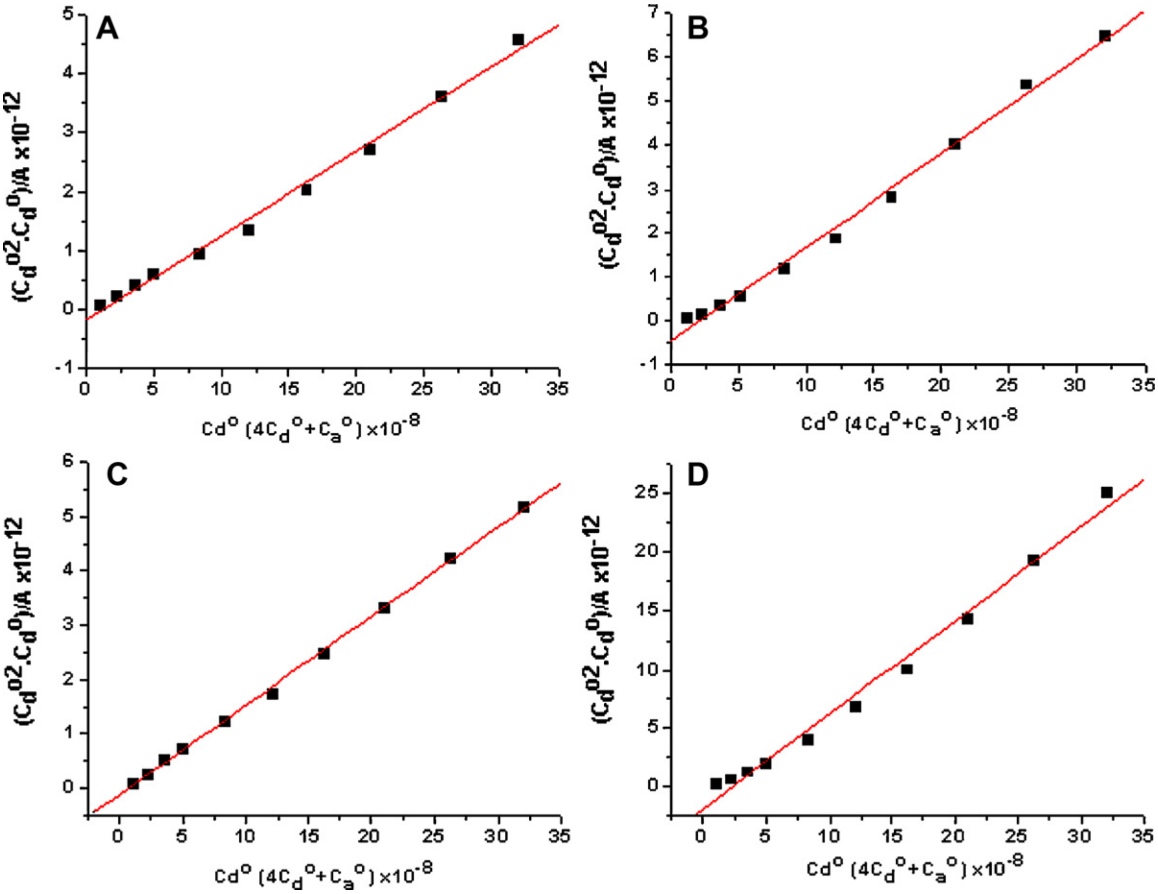


**Fig. 3.** Plot of $((C_a^o)^2C_d^o)/A$ vs. $C_a^o(4C_d^o + C_a^o)$ for the (A) 18C6/p-CHL, (B) 18C6/DDQ, (C) 18C6/CLA, and (D) 18C6/PA systems.

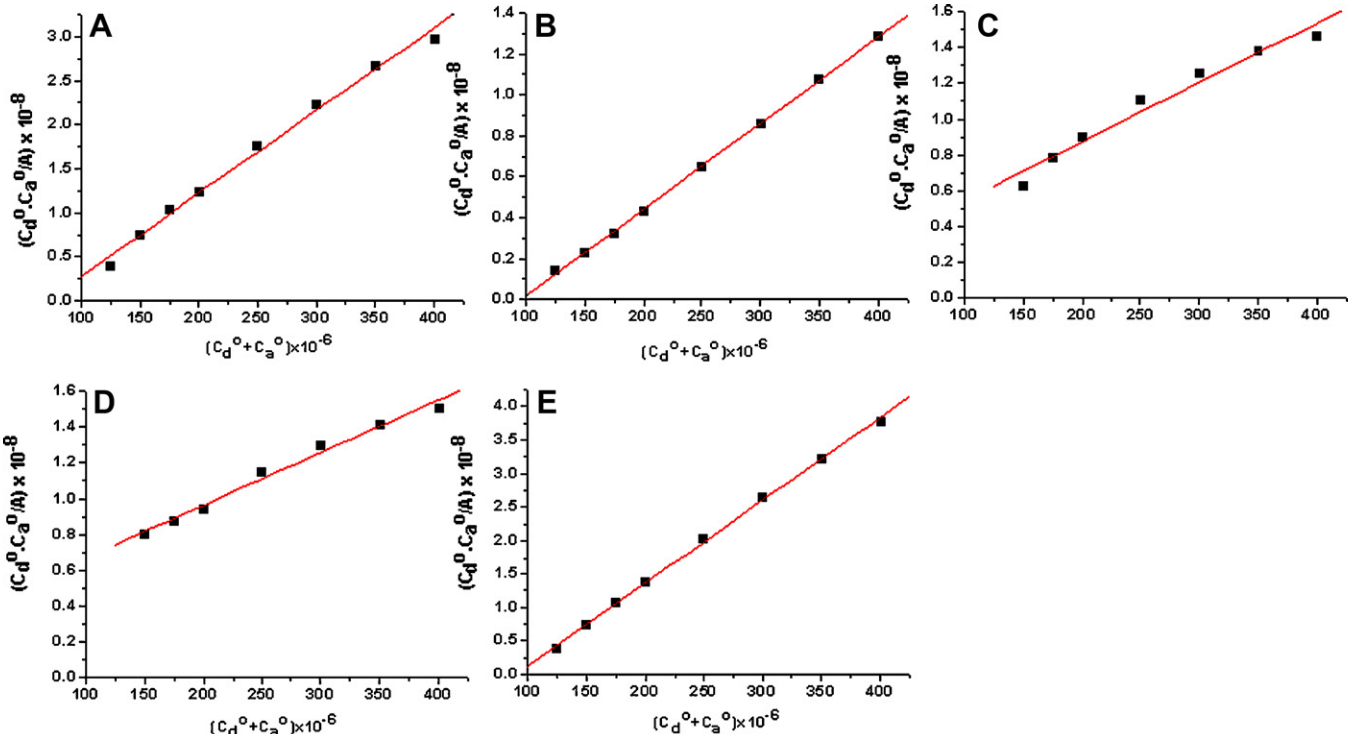


**Fig. 4.** Plot of $C_a^oC_d^o/A$ vs. $C_a^o + C_d^o$ for the (A) 18C6/o-CHL, (B) 18C6/TCNQ, (C) 18C6/DCQ, (D) 18C6/DBQ, and (E) 18C6/NBS systems.

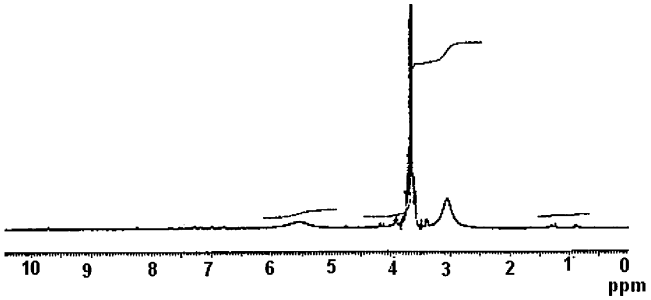


**Fig. 5.** $^1$H NMR spectrum of $[(18C6^{\bullet+})(DDQ^{\bullet-})_2]$ charge transfer complex.

**Table 5**
Characteristic infrared frequencies (cm$^{-1}$) and tentative assignments of TCNQ and $[(18C6^{\bullet+})(TCNQ^{\bullet-})]$ CT complex.

| TCNQ | $[(18C6^{\bullet+})(TCNQ^{\bullet-})]$ | Assignments$^{(b)}$ |
|---|---|---|
| 3137 | 2888 | |
| 3050 | 2795 | $\nu$(C–H) |
| 2969 | 2750 | |
| 2851 | | |
| 2220 | 2171 | $\nu$(CN) |
| | 2129 | |
| 1670 | 1636 | $\nu$(C=C) |
| 1539 | 1598 | |
| – | 1575 | |
| | 1506 | $\delta$(CH) deformation |
| | 1499 | |
| | 1471 | |
| 1352 | 1350 | $\nu$(C–O) |
| 1285 | 1247 | $\nu$(C–N) |
| 1205 | 1106 | $\nu$(C–C) |
| 1118 | | |
| 1044 | | |

plex base on the 1:1 modified Benesi–Hildebrand equation [18], the straight line come from the relationship between $C_a^o C_d^o/A$ vs. $C_a^o + C_d^o$ is drawn in Fig. 4B. The spectrophotometric data of the TCNQ complex are summarized and inserted in Table 1.

Main band assignments for both TCNQ and its CT-complex appeared in the spectra are given in Table 5. A comparison of the relevant IR spectral bands of the free donor, 18C6 and TCNQ acceptor with the corresponding appeared in the IR spectrum of the isolated CT-complex, clearly indicated that the characteristic bands of 18C6 show some shift in the frequencies (Table 5), as well as some change in their bands intensities. This could be attributed to the expected symmetry and electronic structure changes upon the formation of the CT-complex. Moreover, in general, the IR spectrum of the molecular complex of TCNQ with 18C6 indicate the $\nu$(C≡N) and $\nu$(C=C) of the free TCNQ are shifted to lower wavenumber values on complexation. Since TCNQ is deprived from any acidic centers, thus we may conclude that the molecular complexes are formed through n–$\pi^*$ charge migration from HOMO of the donor to the LUMO of the acceptor.

$^1$H NMR spectrum for the $[(18C6^{\bullet+})(TCNQ^{\bullet-})]$ complex (Fig. 6) showed two main signals around 3.6 and 7.2 ppm due to $nCH_2$ of 18C6 and protons of aromatic groups of TCNQ, respectively. All signals are downfield shifted compared to signals of free donor and TCNQ. This shift is due to the ring current influence of the magnetic anisotropy of oxygen atoms and the field effect of the electronic dipoles located on the oxygen atoms.

### 3.5. DCQ, DBQ and NBS

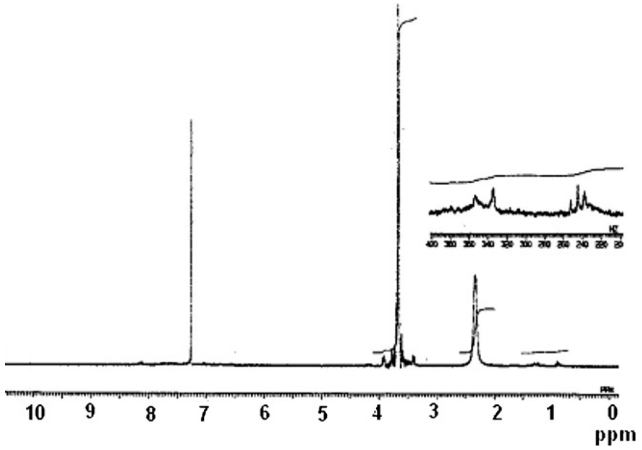


**Fig. 6.** $^1$H NMR spectrum of $[(18C6^{\bullet+})(TCNQ^{\bullet-})]$ charge transfer complex.

The reactions of 18C6 with the DCQ, DBQ and NBS as a $\pi$-acceptors were carried out in methanol except for NBS in chloroform as a solvent. The electronic absorption spectra of the reactants, 18-crown-6 ($1.0 \times 10^{-4}$ M) and acceptors ($1.0 \times 10^{-4}$ M) in MeOH or $CHCl_3$ along with those of the formed 1:1 CT-complexes are shown in Fig. 1E–G, respectively. The spectra demonstrate that the formed CT-complexes have strong absorption bands around 295, 286 and 280 nm for [(18C6)(DBQ)], [(18C6)(DCQ)] and [(18C6)(NBS)] complexes, respectively. These bands do not exist in the spectra of the reactants in the same situations. The stoichiometry of the [18C6]-acceptor reactions was shown in all cases to be of ratio 1:1. This was concluded on the bases of the obtained elemental analysis data of the isolated solid CT-complexes as indicated in Section 2, as well as from the complexes infrared spectra, which indicate the existence of the bands characteristic for both the [18C6] and the respective acceptors. The stoichiometry of 1:1 is also strongly supported by photometric titration measurements. In these measurements concentration of 18-crown-6 was kept fixed, while the concentration of the acceptors was varied over the range of $0.25 \times 10^{-4}$–$4.00 \times 10^{-4}$ M as described in Section 2. Photometric titration curves based on these measurements are shown in Fig. 2E–G. Accordingly, the formed CT-complexes upon the reaction of [18C6] as a donor with the $\pi$-acceptors under investigation in chloroform or methanol have the general formula [(18C6)(acceptor)]. The 1:1 modified Benesi–Hildebrand Eq. (1), was used in calculating the values of the equilibrium constant, $K$ and the molar absorptivity ($\varepsilon$). $C_a^o$ and $C_d^o$ are the initial concentrations of the $\pi$-acceptors (DBQ, DCQ and NBS) and the donor 18C6, respectively, while $A$ is the absorbance of the strong bands around 295, 286 and 280 nm for their CT-complexes. Plotting the values of the $C_a^o C_d^o/A$ against $C_a^o + C_d^o$ values for each acceptor, a straight line is obtained with a slope of $1/\varepsilon$ and intercept of $1/K\varepsilon$ as shown in Fig. 4C–E. The values of both $K$ and $\varepsilon$ associated with these complexes were data obtained throughout these calculations are given in Table 1. These complexes show high values of both the formation constant ($K$) and the extinction coefficients ($\varepsilon$). These high values of $K$ confirm the expected high stabilities of the formed CT-complexes as a result of the expected high donation of the 18-crown-6. The equilibrium constants are strongly dependent on the nature of the used acceptor including the type of electron withdrawing substituents to it such as halo groups. For example, Table 1, the value of equilibrium constant for [(18C6)(DCQ)] is highest value than both [(18C6)(DBQ)] and [(18C6)(NBS)] complexes in respective solvent. This value is about twice and one half times higher than the values of equilibrium constant for the complexes [(18C6)(DBQ)] and [(18C6)(NBS)], respectively, reflecting the relatively higher electron acceptance ability for DCQ. The number of donating atoms available is another important factor that affects the stability of crown-ion complexes [32]. Since in the process of molecular complexation, it

**Table 6**
Characteristic infrared frequencies (cm$^{-1}$) and tentative assignments of DCQ, DBQ, NBS and their CT complexes.

| DCQ | DBQ | NBS | [(18C6)(acceptor)] | | | Assignments$^{(b)}$ |
|---|---|---|---|---|---|---|
| | | | DCQ | DBQ | NBS | |
| 3079 | 3074 | 2973 | 2989 | 2931 | 2990 | |
| 3052 | | 2950 | 2932 | | 2948 | |
| 2954 | | 2939 | | | 2835 | |
| 2925 | | 2927 | | | | ν(C–H) |
| 2869 | | | | | | |
| 2854 | | | | | | |
| 1673 | 1678 | 1716 | 1684 | 1673 | 1684 | ν(C=O) |
| 1618 | 1640 | – | 1635 | – | 1641 | ν(C=C) |
| 1573 | 1605 | | | | | |
| 1510 | 1566 | 1426 | 1542 | 1552 | 1543 | |
| 1464 | 1547 | 1414 | 1471 | 1475 | 1471 | δ(CH) deformation |
| | 1509 | | 1438 | | 1446 | |
| 1376 | 1342 | 1311 | 1398 | 1369 | 1397 | |
| 1366 | 1301 | 1238 | 1368 | 1318 | 1367 | |
| 1305 | 1270 | 1197 | 1316 | 1226 | 1316 | |
| 1285 | 1143 | 1167 | 1267 | 1147 | 1267 | |
| 1274 | 1013 | 1157 | 1227 | 1080 | 1227 | |
| 1162 | 1002 | 1007 | 1180 | 1036 | 1183 | |
| 1044 | 902 | – | 1144 | | 1144 | ν(C–O) + ν(C–N) |
| 917 | 869 | | 1078 | 918 | 1078 | ν(C–C) + ν(C–X) |
| 898 | | | 1023 | 835 | 1035 | |
| | | | 919 | | 1023 | |
| | | | 837 | | 918 | |
| | | | | | 835 | |

is reasonably assumed that the charge density is donated from the donor to acceptor, the increased number of crown oxygens in the ring is expected to increase the crown-acceptor interaction in solution. The effective overlapping of donor–acceptor orbitals involves the proper spatial positions of donor and acceptor molecules. This also needs specific conformation of donor. If the conformation of donor in the complexes form differs significantly from, it's most stable conformation in the Free State. During complexation, some energy will consume for the conversion of most stable conformation of free donor to a conformation which is suitable for complex formation. This will act as a destabiliser factor in the whole process. Among the donor studied, 18C6 has the most rigid structure. So, the variation of its conformation involves energy consumption. Based on this property, the observation of least stability for [(18C6)(DBQ)] (Table 1) is not unexpected.

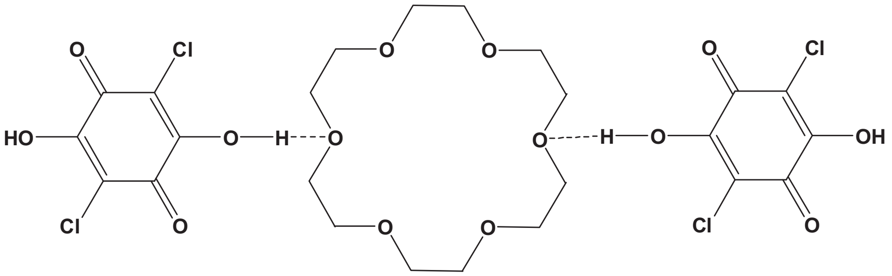
The conductance as a function of [acceptor]/[18C6] mole ratios was measured and the results are shown that there is no increase of conductance upon acceptor (DBQ, DCQ and NBS) addition thus, it can be concluded that the complexes are completely nonionic.

IR spectra of 18C6 and their 1:1 [(18C6)(DCQ)], [(18C6)(DBQ)] and [(18C6)(NBS)] charge transfer complexes are compared in Table 6. The bands generally show some shifted upon complexation for the stretching vibrations of the carbonyl group and C–X (where X = Cl or Br).

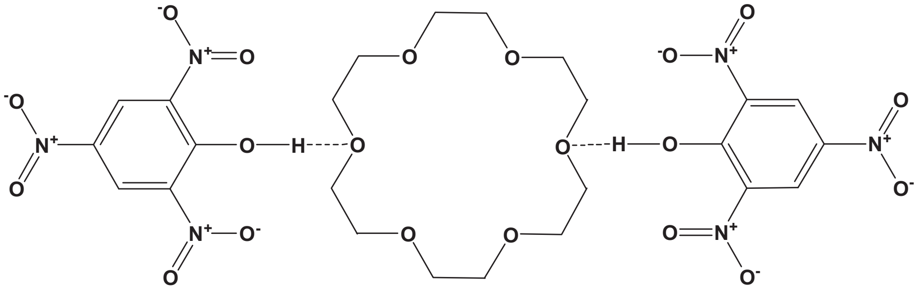
### 3.6. CLA and PA

Electronic spectra were recorded in the region 200–800 nm. New detected bands in the UV–visible spectra at 308 and 421 nm are observed immediately on mixing solutions of 18-crown-6 and each of the chloranilic and picric acids in chloroform, respectively. The electronic absorption spectra of the donor (18C6) with acceptors (CLA and PA) have molar ratios (donor:acceptor) 1:2. Fig. 1H and I, revealed strong absorption bands attributed to the CT interaction. The spectrum of the 18C6/CLA system shows one strong absorption band at 308 nm with hyperchromic shift due to the formation of [(18C6)(CLA)$_2$] CT complex, while the corresponding absorption bands associated with the formation of the complex [(18C6)(PA)$_2$] is observed at 421 nm (red shift) in the spectrum of 18C6/PA system. Furthermore, photometric titration measurements based on the characteristic absorptions bands of the CT complexes (Fig. 2H and I) confirmed the molar ratios of the two mentioned complexes. Photometric titrations between 18-crown-6 and both of CLA and PA in CHCl$_3$ solvent were carried out as follows: concentration of 18C6 ($C_d$) were kept fixed at $1.0 \times 10^{-4}$ M, whereas that of the acceptor (CLA or PA) $C_a$ was changed over a wide range of $0.25 \times 10^{-4}$–$4 \times 10^{-4}$ M. The peak absorbances appeared in the spectra that assigned to the formed CT complexes were measured and plotted as a function of the ratio $C_d$:$C_a$ according to the known method [17]. The 1:2 modified Benesi–Hildebrand Eq. (2) was used to calculate the values of the equilibrium constant, $K$ (l mol$^{-1}$) and the extinction coefficient, $\varepsilon$ (l mol$^{-1}$ cm$^{-1}$) for both complexes. The data obtained throughout this calculation are given in Table 1. Plotting values of $(C_a^o)^2 C_d^o/A$ vs. $C_a^o(C_a^o + 4C_d^o)$ values of Eq. (2), straight lines are obtained with a slope of $1/\varepsilon$ and intercept of $1/K\varepsilon$ as shown in Fig. 3C and D. Table 1, have the calculated values of the spectroscopic data like; $\varepsilon$, $K$, $\mu$, $R_N$, $\Delta G$, $I_p$ and $f$, which deduced from Eqs. (3)–(8). Generally, these complexes show high values of both the formation constant ($K$) and the molar absorptivity ($\varepsilon$). These high values of $K$ confirm the expected high stabilities of the formed CT-complexes as a result of the expected high donation of the 18-crown-6. The equilibrium constants are strongly dependent on the nature of the used acceptor including the type of electron withdrawing substituents to it such as nitro and halo groups.

The band assignments of infrared spectra of the donor (18C6) as well as the formed CT complexes 18C6/CLA and 18C6/PA are reported in Table 7. However, the appearance of a group of IR spectral bands in the spectra of the CT complexes supports the conclusion that a deformation of the electronic environment of 18C6 is occurred by accepting protons from CLA or PA. The IR spectra of the two CT complexes of PA and CLA are characterized by a group of bands appearing in the region >3400 cm$^{-1}$, which are not appearing in the spectra of the free donor and acceptors. These bands are attributed to the stretching vibration of the intermolec-



**Formula II.** Suggested structure of [(18C6)$(CLA)_2$] complex.



**Formula III.** Suggested structure of [(18C6)$(PA)_2$] complex.

ular hydrogen bond [33]. These results caused to the protonation of the $^{+}$OH group of the donor from two sides, through protons transfer from the acidic center on the CLA acceptor. On the other hand the intermolecular hydrogen bond occurs in PA acceptor from –OH group to the basic center oxygen atoms atom. The shift of the IR bands of the acceptor part to lower wavenumbers and those of the donor part to higher values reflects a donor to acceptor charge transfer of n–π* interaction, $D_{HOMO} \rightarrow D_{LUMO}$ transition [34]. Accordingly, the hydrogen bonding between the donor and the acceptors can be formulated as Formulas II and III. The equivalent conductance values at $1.0 \times 10^{-4}$ molar concentrations indicated that these complexes have a small limit of conductivity. The data of conductivity confirms that these complexes have a positive ($^{+}$OH) and negative charge ($O^{-}$ of acidic in chloranilic or picric acid) resulted from CT transition. The low conductivity values for the two CT-complexes may be due to intermolecular hydrogen bond formation.

**Table 7**
Characteristic infrared frequencies (cm$^{-1}$) and tentative assignments of CLA, PA and their CT complexes.

| CLA | PA | [(18C6)(acceptor)] | | Assignments$^{(b)}$ |
|---|---|---|---|---|
| | | CLA | PA | |
| – | – | 3509 | 3447 | Hydrogen bond |
| 3235 | 2980 | 3022 | 3080 | |
| | 2872 | 2853 | 2962 | ν(C–H) |
| | | | 2742 | ν(O–H) |
| | | | 2664 | |
| 1664 | 1861 | 1696 | 1709 | ν(C=O) |
| 1630 | 1632 | 1664 | 1667 | ν($NO_2$) |
| | 1608 | 1625 | 1618 | ν(C=C) |
| – | 1529 | 1591 | 1532 | |
| | 1432 | 1566 | | δ(CH) deformation |
| | | 1519 | | |
| 1368 | 1343 | 1456 | 1434 | |
| 1263 | 1312 | 1439 | 1337 | |
| 1207 | 1263 | 1382 | 1264 | |
| 1168 | 1150 | 1345 | 1237 | |
| 981 | 1086 | 1317 | 1159 | |
| 851 | 917 | 1296 | 1075 | |
| 752 | 829 | 1269 | 1053 | |
| 690 | 781 | 1236 | 933 | |
| 569 | 732 | 1201 | 906 | ν(C–O) + ν(C–N) |
| | 703 | 1130 | 866 | ν(C–C) + ν(C–X) |
| | 652 | 1054 | 833 | δ($NO_2$) |
| | 522 | 981 | 785 | |
| | | 886 | 707 | |
| | | 837 | 580 | |
| | | 977 | 546 | |
| | | 628 | | |
| | | 571 | | |
| | | 538 | | |
| | | 500 | | |

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