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Preparation, spectroscopic and antibacterial studies on charge-transfer complexes of 2-hydroxypyridine with picric acid and 7,7`,8,8`-tetracyano-*p*-quinodimethane

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Abstract

The reactions of electron acceptors such as picric acid (HPA) and 7,7`,8,8`-tetracyano-*p*-quinodimethane (TCNQ) with 2-hydroxypyridine (HPyO) have been investigated in EtOH at room temperature. Based on elemental analysis and IR spectra of the solid CT-complexes along with the photometric titration curves for the reactions, the data obtained indicate the formation of 1:1 charge transfer complexes [(H_2PyO)(PA)] and [(PyO)(HTCNQ)], respectively. The infrared and ^{1}H NMR spectroscopic data indicate a charge transfer interaction associated with a proton migration from the acceptor to the donor followed by intramolecular hydrogen bonding in [(H_2PyO)(PA)] complex. Another charge transfer interaction was observed in [(PyO)(HTCNQ)] complex. The formation constants (K_{CT}) for the CT-complexes are shown to be strongly dependent on the type and structure of the electron acceptors**.** Factors affecting the CT-processes and the kinetics of thermal decomposition of the complexes have been studied. The CT complexes were screened for their antibacterial activities against selected bacterial strains.

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Key words: Charge transfer; 2-Hydroxypyridine; Electron acceptors; UV-visible; IR; ^{1}H NMR; TGA spectrometry; Kinetics of thermal decomposition; Antibacterial activity.

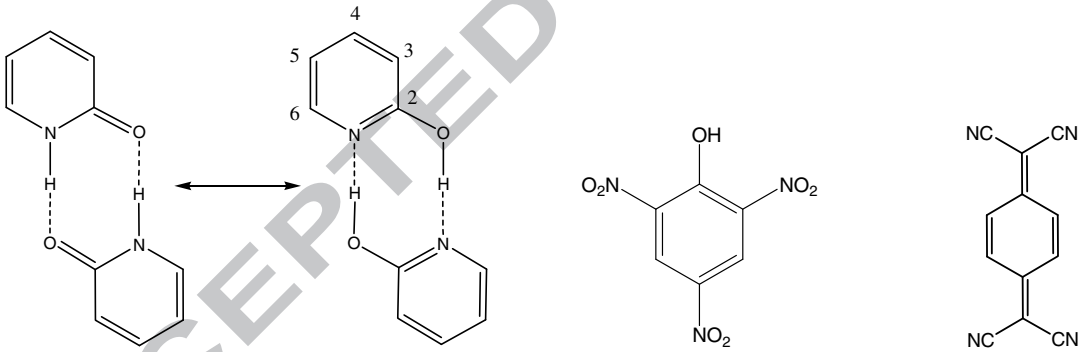
1. Introduction

Organic charge-transfer complexes [1-3] are of great importance in many chemical reactions including addition, substitution, condensation [4, 5], biochemical and bio-electrochemical energy-transfer processes [6] and biological systems [7]. The charge-transfer complexes that are formed between *n*- and π-donors [1-3, 8-10] exhibit certain properties which could be important in biological systems and other various applications in electronics, solar cells, and optical devices [11-12].

Proton transfer reactions are important in many chemical and biological systems [13-16]. It constitutes one of the simplest models for DNA base units and for molecules involved in biological life cycles, where proton transfer causes genetic damage [17]. For some hydrogen bond, particular type of proton transfer occurs in systems where catalysis molecules can conduct the process by serving as a bridge between the donor and acceptor sites [18].

The donor molecule used in this study was 2-hydroxypyridine (HPyO), an aromatic heterocyclic compound representing a very important class of compounds which possess a system of π- and *n*-electrons. Regarding to the equilibrium between 2-pyridone and 2-hydroxypyridine, it is clear that this tautomerism is ruled by a proton transfer between nitrogen and oxygen, **I**. This system in principle is able to form two types of charge-transfer complexes [19–23]. The πelectron acceptors 7,7',8,8'-tetracyanoquinodimethane (TCNQ) and picric acid (HPA) are known to form stable colored CT-complexes with many donor bases [1, 24-27].

The increased interest in the study of charge-transfer interactions stems from the various applications of CT-complexes [1, 28]. We have been studying the synthesis and spectroscopic characterization of a variety of molecular donors and acceptors in order to fully understand the nature of their CT interactions [29-35]. In continuation of our previous studies made on the charge transfer complexes of the donor 2-hydroxypyridine [35], we wish to report on the results of preparation and spectroscopic investigation of the interaction of 2-hydroxypyridine (HPyO) as an electron donor with picric acid (HPA) and 7,7`,8,8`-tetracyano-*p*-quinodimethane (TCNQ) as electron acceptors to characterize the reaction products. This investigation contributes to a deeper understanding of the mode of interaction, reaction stoichiometries and structures in the different kinds of the charge-transfer complexes under investigation. Furthermore, the results obtained here give some insight of analogous reactions with other related derivatives of *n*-donor bases.



2-Pyridone 2-hydroxypyridine (HPyO) HPA TCNQ

I. Structure of the donor and acceptors

2. Experimental

2.1. Materials and spectral measurements

All the used chemicals were of high grade. 2-Hydroxypyridine (HPyO) was obtained from

Aldrich, Picric acid (HPA) was obtained from BDH while 7,7`,8,8`-tetracyano-*p*-quinodimethane (TCNQ) was purchased from Merck Chemical Co.

The electronic absorption spectra were recorded in the region of 250□900 nm using UV-Vis. spectrophotometer model JASCO V-530 with quartz cell of 1.0 cm path length. The infrared spectra of the reactants and the obtained complexes were recorded using KBr discs on Perkin-Elmer 1430 ratio recording Infrared spectrometer. ^{1}H NMR spectra were recorded on Varian spectrophotometer Gemini 200 operating at 200 MHz using dimethylsulphoxide-d_6 as a solvent and TMS as an internal reference.

Photometric titrations at (354, 400 nm) and (743, 845 nm) were performed for the reactions of HPA and TCNQ, respectively, with the donor (HPyO) in Ethanol at 25 ^{o}C using a Helios Gamma Unicam UV-Vis. Spectrophotometer and Jenway Visible range spectrophotometer model 6300 as follows. The concentrations of HPyO (C_d) were kept fixed at 1.00×10^{-4} mol/L in the reaction with the acceptors HPA and TCNQ. Whereas the concentrations of the acceptors C_a were changed over a wide range of: $0.25 \times 10^{-4} - 3.00 \times 10^{-4}$ mol/L for all acceptors, Table 1. The acceptor-donor molar ratio ($C_a : C_d$) obtained in this case varies over the range 0.25:1.00 to 3.00:1.00. The peak absorbances appeared in the spectra that assigned to the formed CT-complexes were measured and plotted as a function of the ratio $C_a : C_d$ according to the known method [36], Table 2.

Elemental analyses of the dried and pure samples were carried out in microanalysis unit of Cairo University, Egypt using CHNS-932 (LECO) and Vario EL elemental analysers. Chlorine was determined by burning the substance in oxygen with platinum contact and following titration with mercuric nitrate towards diphenylcarbazide. The results of elemental analyses of the solid

complexes were in accordance with the stoichiometric ratios obtained from photometric titrations.

Thermal analyses (TG, DTG) were carried out using a Shimadzu TGA-50 H computerized thermal analysis system. The system includes program which process data from the thermal analyzer with the ChromotPac C-R3A. The rate of heating of the samples was kept at 10 ^{o}C/min. Sample masses 2.066, 2.896 and 1.967 mg for HPyO and [(H_2PyO(PA)] (**1**) [(PyO)(HTCNQ)] (**2**) complexes, respectively were analyzed under N_2 flow at 20 ml/min.

<<<< Insert tables 1, 2 >>>>>

2.2. Preparation of the solid complexes

*[(H_2PyO(PA)] (**1**)*

To a solution of HPyO (95.1 mg, 1.0 mmol) in EtOH (10 mL), a solution of HPA (458.2 mg, 2.0 mmol) in EtOH (50 mL) was added at room temperature with stirring. The formed scarlet yellow precipitate was filtered off and washed with EtOH (3 × 1/2 mL). The precipitate was also washed with Et_2O (2 × 1/2 mL) and dried in vacuo overnight over $CaCl_2$. Yield: 295.0 mg (90.15 %).

Anal. found (Calcd. for $C_{11}H_8N_4O_8$, 324.20): C**,** 40.98 (40.75); H, 2.61 (2.49); N, 17.09 (17.28).

[(PyO)(HTCNQ)] (**2**)

To a solution of HPyO (95.1 mg, 1.0 mmol) in EtOH (10 mL), a saturated solution of TCNQ (205 mg, 1.0 mmol) in EtOH (90 mL) was added. The resultant green solution was stirred for about 6 h. The volume of the reaction mixture was reduced to half then, left overnight to obtain the dark green precipitate of complex **2**, which was filtered off, washed with EtOH (3 ×1/2 mL) and dried in vacuo over $CaCl_2$. Yield: 150.0 mg (50.12 %).

Anal. found (Calcd. for $C_{17}H_9N_5O$, 299.29): C**,** 68.45 (68.22); H, 3.20 (3.03); N, 23.37 (23.40).

Preparation of (H_2PyO)Cl

To a solution of HPyO (19.0 mg, 0.20 mmol) in MeOH (10 mL), HCl was added (0.40 mmol, 0.10 M) drop by drop with continuous stirring. By evaporation of solvent, the solid 2-hydroxybipyridine-1-ium chloride was obtained.

Anal. found (Calcd. for C_5H_6ClNO, 131.56): C**,** 45.57 (45.65); H, 4.71 (4.60); N, 10.57 (10.65); Cl, 27.32 (26.95).

2.3. Antibacterial activity

The *in vitro* antibacterial screening effects of the compounds were tested against four bacterial strains namely *Escherichia coli* and *Pseudomonas aeroginosa* (Gram negative bacteria) and *Bacillus subtillis* and *Staphylococcus aureus* (Gram positive bacteria) by agar well diffusion method using nutrient agar medium for antibacterial activity [37-40]. All bacteria were inoculated into Nutrient Broth and incubated for 24 *h* (1.0 mL of inocula were added to 50 mL of agar media (50 ºC) and mixed). The agar was poured into 120 mm petri dishes and allowed to cool to room temperature. In the agar well diffusion method, the dilution plate method was used to enumerate microorganisms for 24 *h* [41, 42]. By using a sterilized cork borer (7 mm diameter), wells were dug in the culture plates. 0.1 mL of the compounds dissolved in DMSO (250 µmol/mL) were added to these wells. The petri dishes were left at 5 ºC for 2 *h* and then the plates were incubated at 35 ºC for bacteria (22–24 *h*). At the end of the period, inhibition zones formed on the medium were evaluated in milimeters (mm). DMSO was used as a control under similar conditions for comparison (0.1 mL). The results were compared with a similar run of standard Ampicilin as antibacterial. The zones of inhibition based upon zone size around the wells were measured and calculated as a mean of three replicates.

3. Results and discussion

Two stable charge-transfer complexes, [(H_2PyO)(PA)] (**1**) and [(PyO)(HTCNQ)] (**2**) with the molar ratio of 1:1 (donor-accpetor) are obtained in good yields during the reaction of HPyO in EtOH with HPA and TCNQ, respectively. This molar ratio was determined from the photometric titration curves and in good agreement with the analytical data obtained from elemental analyses.

3.1. Electronic spectra

Electronic absorption spectra of 2-hydroxypyridine donor (HPyO) and its obtained CT-complexes (Fig. 1(A, B)) revealed strong absorption bands attributed to the CT-interaction. These bands are not present in the spectra of the free reactants and observed at (354, 410 nm) and (743, 845 nm) for the complexes [(H_2PyO)(PA)] (**1**) and [(PyO)(HTCNQ)] (**2**), respectively. The interaction of the donor with the π-acceptor in polar solvents such as ethanol, complete electron transfer takes place with the formation of intensively coloured radical ions. The interaction of HyO with HPA and TCNQ at room temperature gave coloured chromogens showing different absorption maxima at (354, 410 nm) and (743, 845 nm) for HPA and TCNQ, respectively. The predominant chromogen with TCNQ in EtOH is the bluish-green coloured radical ion, which exhibits strong absorption maxima at 845 and 743 nm [1, 2, 24-27].

Furthermore, photometric titration measurements based on the characteristic absorption bands of the CT-complexes, Fig. 2(A, B) confirmed the complex formation in a ratio, HPyO: acceptor = 1:1. Examination and comparison of the absorption spectra of the HPyO-acceptors system reveal that the spectra are characterized by maxima at the defined wavelengths which are nearly similar to the same absorption bands of such acceptors with other donors [24-27, 34, 35].

The obtained spectrophotometric data, Table 2 were used to calculate the values of both equilibrium constant, K_C, and extinction coefficient, ε of the CT-complexes in EtOH for complexes **1** and **2** based on the known equation (1) for the 1:1 stoichiometry [43].

$$\frac{C_d^\circ \cdot C_a^\circ}{A} = \frac{1}{\varepsilon K_c} + \frac{C_d^\circ + C_a^\circ}{\varepsilon} \qquad (1)$$

where C_a° and C_d° are the initial concentration of the acceptor and the donor, respectively, and A is the absorbance of the CT band. Plotting $C_d^\circ . C_a^\circ / A$ vs ($C_d^\circ + C_a^\circ$) for the complexes **1**and **2,** straight lines were obtained supporting our conclusion of the formation of the 1:1 complexes, Fig. 3(A,B). In these plots, the slope and intercept for each case equal 1/ε and 1/εK_C, respectively. The values of both K_C and ε associated with the complexes are given in Table 3. These data reveals that [(PyO)(HTCNQ)] (**2**) complex shows a higher value of the formation constant (K_C) in comparison with [(H_2PyO)(PA)] (**1**) complex. This confirms the expected high stability of complex **2** as a result of the expected higher accepting properties of TCNQ compared with picric acid. The values of the equilibrium constants are dependent on the nature of the acceptor including the type of electron withdrawing substituents such as cyano and nitro groups.

<<<< Insert Figs 1, 2,3 >>>>>

3.2. Determination of the spectroscopic and physical data of CT-complexes

The oscillator strength (*f*) of the CT absorption spectra in ethanol at room temperature was obtained from the approximate formula [44].

$$f = 4.319 \times 10^{-9} (\varepsilon_{max} \cdot \Delta \upsilon_{1/2}) \qquad (2)$$

where $\upsilon_{1/2}$ is the band-width for half-intensity in cm^{-1} and ε_{max} is the maximum extinction coefficient of the CT-band. The oscillator strength values are given in Table 3. The data resulted

reveals several items: The HPyO–HPA and HPyO–TCNQ systems show different values of both formation constant (K_c) and molar absorptivity (ε). The different values of the oscillator strength, f, increase with increasing the accepting property of the acceptor. This result could also be explained on the basis of competitive solvent interactions with the acceptors [29-35].

The transition dipole moment (μ) which determines the transitions from a donor π-bonding orbital to an acceptor π^* anti-bonding orbital is calculated [45] according to equation 3 and is given in Table 3.

$$\mu_{(Debye)} = 0.958\left(\frac{\varepsilon_{\max} \cdot \Delta\upsilon_{1/2}}{\upsilon_{\max}}\right)^{1/2} \qquad (3)$$

The ionization potential (I_p) of the HPyO donor in the charge transfer complexes **1** and **2** are calculated using empirical equation 4 derived by Aloisi and Piganatro [46];

$$I_{D(eV)} = 5.76 + 1.53\times10^{-4} \cdot \upsilon_{CT} \qquad (4)$$

where υ_{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 n–π and π–π interactions between HPyO and acceptors were calculated using equation 5 [45];

$$E_{CT} = (h\upsilon_{CT}) = 1243.667 / \lambda_{CT(nm)} \qquad (5)$$

where, λ_{CT} is the wavelength of the complexation band of the studied complexes.

The standard free energy changes of complexation (ΔG^o) were calculated from the formation constants by the following equation 6 [47];

$$\Delta G^\circ = -2.303RT \log K_{CT} \qquad (6)$$

where R is the gas constant (8.314 J□K^{-1}□mol^{-1}), T is the temperature in Kelvin degrees and K_C is the formation constant of the complexes at room temperature (L mol^{-1}). ΔG^o of interactions are negative in all CT complexes which indicate endothermic processes and reactions are spontaneously proceeding to the direction of CT complex formations, Table 3.

<<<< Insert table 3 >>>>>

3.3. IR Analysis

Assignments of the well characterized bands in the infrared spectra of reactants and the obtained products are given in Table 4. The formation of CT-complexes during the reaction of HPyO with picric acid and TCNQ is strongly supported by observing of the main infrared bands of the donor (HPyO) and acceptors (HPA and TCNQ) in the product spectra. However, the bands of the donor and acceptors in the complexes spectra reveal small shifts in intensities compared with those of the free donor and acceptors. This should be attributed to the expected symmetry and electronic structure changes upon the formation of CT-complexes.

In general for acid-base interaction, a proton transfer from the acceptor (picric acid) to the donor (base) is expected to occur. Such assumption is strongly supported by the appearance of a new band of medium intensity in the spectrum of complex **1**. This band is observed at 3100 and 3047 cm^{-1} for the HPyO–HPA CT-complex, and should be due to the ν(N–H) stretching vibration of hydrogen against positively charged nitrogen [48-52]. The complex spectrum revealed also a broad absorption lying in the region of 2365cm^{-1} and could be attributed to the expected hydrogen bonding in the complex [48]. Depending on these observations, we may suggest that, the acid–base interaction is associated with a proton migration followed by hydrogen bonding formation. The HPyO–HPA interaction involves nitrogen protonation.

Accordingly, we may formulate complex **1** as [($HPyOH^+$)(PA^-)]. The dipole caused by the semipolar N-O bond makes the band position, especially the antisymmetric stretching vibration $\nu_{as}(NO_2)$ sensitive for polar influences and the electronic states of the nucleus. Therefore, one could attribute the shift to a lower wavenumber of $\nu_{as}(NO_2)$ vibration (1535 cm^{-1}) in the [(H_2PyO)(PA)] (**1**) complex spectrum compared with its value in the free HPA (1607 cm^{-1}) due to the increased electronic density on the picrate unit as a result of charge transfer interaction and deprotonation of picric acid upon complexation [49].

The IR spectrum of the free TCNQ shows CN stretching frequency at 2222 cm^{-1}. The significant shift of this vibration toward a different frequency (2252 cm^{-1}) on complexation is indicative of charge transfer from HPyO to π^* of TCNQ and more than one type of CN group might be found. Because TCNQ lacks acidic centers, the molecular complexes can be concluded to form through π-π^* and/or n-π^* charge migration from the HOMO of the donor HPyO to the LUMO of the acceptor TCNQ. The π-π^* CT complex is formed via the benzene ring (electron-rich group) of the HPyO and the electron acceptor (TCNQ) reagents [53, 54]. The cyano group (–C≡N) is an electron-withdrawing group that exists in TCNQ in a conjugated bonding system. The CN groups in TCNQ withdraw electrons from the aromatic ring, and such a process will make the aromatic ring an electron-accepting region. The π^* electron density in CN appears to increase and more easily accept a proton from the donor because of the electron-withdrawing process and the conjugated electron system. So, the interactions mode between HPyO and the TCNQ acceptor occurs through the migration of a H^+ ion to one of the cyano groups in the acceptor to form a positive ion (–C≡N– H^+) that associates with the anion to form ion pairs [55, 56].

Hydrogen bond formation was confirmed with observation of medium broad bands around 3400 cm^{-1} in the vibrational region of ν(O–H) and medium to week broad bands around 2366 cm^{-1} in the vibrational region of ν(N–H).

<<<< Insert table 4 >>>>>

3.4. ^{1}H NMR spectra

The ^{1}H NMR spectra of the reactants and the formed CT-complexes in dmso-d_6 were obtained and the chemical shifts in ppm for all peaks observed in the spectra are given in Table 5. The aromatic protons in the free 2-hydroxypyridine, picric acid and TCNQ were assigned. The ^{1}H NMR spectra of the complexes reveal several observations. All the observed peaks in the spectra of the individual components are also present in the complexes spectra suggesting their formation. The proton signals of the donor HPyO are downfield shifted to higher ppm values indicating a charge migration from the donor towards the acceptors.

In the ^{1}H NMR spectrum of complex **1**, the signal due to the phenolic proton in the free acceptor (HPA) was disappeared in the complex spectrum indicating deprotonation. Instead a new peak is observed in the complex spectrum around 5.00 ppm and assigned to N^{+}–*H* proton indicating protonation of the donor HPyO. This interaction mode was strongly supported by obtaining a similar ^{1}H NMR spectrum for the protonated 2-hydroxypyridinium unit in the compound (H_2PyO)Cl [30, 57, 58].

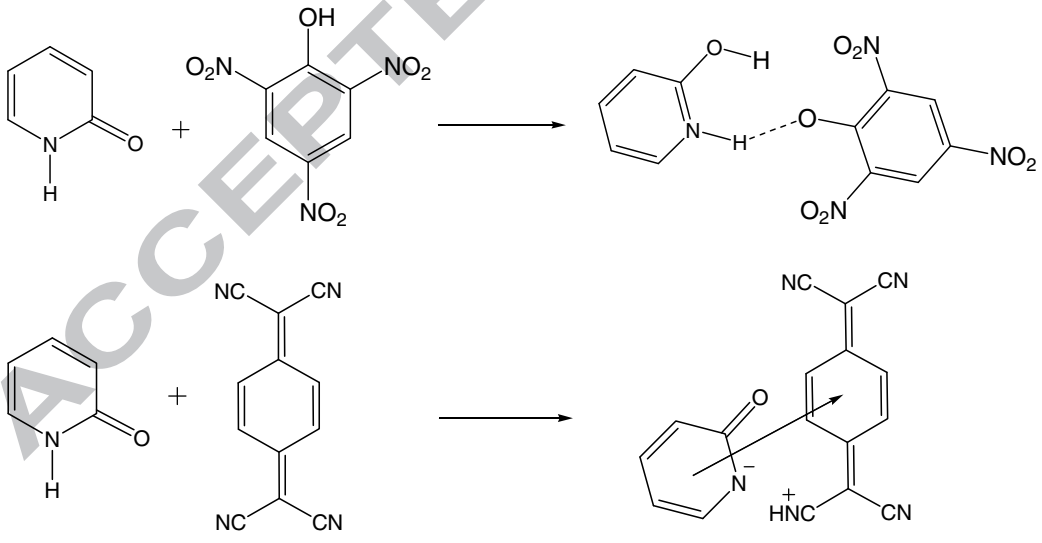
<<<< Insert table 5 >>>>>

The ^{1}H NMR spectrum for complex **2** that formed between HPyO and TCNQ is summarized in Table 5. The spectrum indicated a charge transfer interaction between HPyO and

TCNQ, the proton of N1-*H*/ O2-*H* in HPyO is transferred to nitrogen atom of (C≡N) in TCNQ to form an ion-pair compound, namely (2-cyano-2-(4- (dicyanomethylene) cyclohexa-2,5-dienylidene) ethylidyne) 2-oxopyridinium.

This mode of interaction was confirmed by the absence of the singlet signal of N1-*H*/O2-*H* proton in the free HPyO and appearance of new singlet signal at 6.78, due to N^{+}-*H* proton in the complex spectrum. This new signal was not observed in the spectrum of the free TCNQ, which indicated that the proton of N1-*H*/O2-*H* in the free HPyO and C≡N group primarily involved in the formation of CT complex between HPyO and TCNQ. Transfer of hydrogen proton from HPyO to one of the four C≡N groups in TCNQ resulted in formation of positive ion (C≡N^{+}-*H*) which associated with the anion (PyO^{-}).

Finally, we could suggest that the interaction of 2-hydroxypyridine as a donor with picric acid and 7,7`,8,8`-tetracyano-*p*-quinodimethane (TCNQ) proceeds in a molar ratio of 1: 1 according to the following equations:



3.5. Thermal analysis

To make sure about the proposed structures for the complexes under investigation, thermogravimetric analyses TGA and DTG (Fig. 4) are measured under nitrogen flow. The thermal data obtained for complexes **1** and **2** together with the donor HPyO are summarized and given in Table 6.

The decomposition reaction of complex **1** occurs in one unexpecting stage with a weight loss value of 99.99 % at a temperature of approximately 237 ^{o}C. This stage of decomposition might be associated with the total loss of complex molecule in good agreement with the calculated value of 100.00 %.

The obtained data for complex **2** indicate that, the decomposition reactions occur in two stages. The donor molecule, PyO^{-} is lost at a temperature maximum of 137 ^{o}C. The calculated weight loss of PyO^{-} unit in this complex corresponds to 31.44 % in agreement with the obtained value of 30.50 %. The second stage of decomposition proceeds at a maximum temperature of approximately 265 ^{o}C and associated with a weight loss value of 68.50 %. This could be attributed to the loss of the protonated acceptor unit, $TCNQH^{+}$ in agreement with the calculated values of 68.56 %.

<<<< Insert Fig. 4, table 6 >>>>>

3.6. Thermodynamics parameters of the thermal decomposition of the complexes

It is well known that the temperature has a great influence on any chemical process. So that, it may enhance or retard such dependence on the nature of the reactants and/or the products. The thermodynamic parameters, namely; the equilibrium constants (K_c), the enthalpy (ΔH), the Gibbs free energy (ΔG) and the entropy (ΔS) were calculated using the following equations [59-63]

$$\Delta G = -RT \ln K_c \quad (7)$$

$$\log K_c = \Delta S/2.203R - \Delta H/2.303RT \quad (8)$$

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

where R is an ideal gas constant (8.314 J□K^{-1}□mol^{-1}) and T is the absolute temperature (in K). Plotting log K_c against 1/T gives straight lines, (Fig. 5) with slope and intercept equal $-\Delta H/2.303R$ and $\Delta S/2.303R$ were calculated. The thermodynamic parameters are reported in Table 7.

The calculated data indicates the high values of entropy (ΔS) and enthalpy (ΔH) and low values of the Gibbs free energy change (ΔG). This may be attributed to the ease of decomposition of complexes **1** and **2** in comparison with the free donor. The positive values of ΔH confirm the endothermic nature of compounds and the decomposition of chemical bonds. The positive values of ΔS indicate a less orderly structured.

<<< Insert Table 7 >>>

<<< Insert Fig. 5 >>>

3.7. Antibacterial activity

The *in vitro* antibacterial activity of the donor and its CT complexes were tested against four bacterial strains, *Bacillus subtillis* and *Staphylococcus aureus* as gram positive bacteria and *Escherichia coli* and *Pseudomonas aeroginosa* as gram negative bacteria by agar well diffusion method, Table 8.

The activity was determined by measuring the inhibition zone diameter values (mm) of the complexes against the early mentioned microorganisms. Ampicilin was used as a positive control. The screening data are reported in Table 8. The results indicated that the HPyO complexes showed varying degrees of inhabitation against the tested bacterial species. Regarding the inhabitation zone

diameter, complex **1** had the highest antibacterial activity against the growth of the tested bacterial species compared to complex **2**. It gained approximately 69% of activity of tested antibiotic (Ampicilin). Complex **1** exhibited moderate inhibitory results against the tested Gram-positive and low inhibitory results against Gram-negative bacterial species. The marked activity of complex **1** might be due to the outer membrane of the tested bacterial species is more permeable for complex **1** than complex **2** [64-67].

<<<< Insert table 8 >>>>>

4. Conclusion

The interactions between the electron donor HPyO with the acceptors picric acid (HPA) and 7,7',8,8'-tetracyanoquinodimethane (TCNQ) were studied spectrophotometrically in ethanol. New charge-transfer complexes were isolated and characterized using microanalyses, electronic, IR, and ^{1}H NMR, spectra as well as thermal and kinetic thermodynamic studies. The stoichiometry of the products was found to be 1:1 in both cases. Accordingly, the formed CT-complexes have the formulas [(H_2PyO)(PA)] (**1**) and [(PyO)(HTCNQ)] (**2**). The antibacterial activity test results showed that complex **1** have antibacterial activity against some bacterial strains.

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Table 1.
Molar concentrations for HPyO with the acceptors in the reaction mixtures

Base conc., $\times 10^{-4}$ M	Acceptor	Concentration range of the acceptors, M	Acceptor-base molar ratio
1.00	HPA	$0.25 \times 10^{-4} - 3 \times 10^{-4}$	0.25: 1.00 – 3.00:1.00
1.00	TCNQ	$0.25 \times 10^{-4} - 3 \times 10^{-4}$	0.25: 1.00 – 3.00:1.00

Table 2.
The Values of $C_d^\circ . C_a^\circ / A$ and $C_d^\circ + C_a^\circ$ for complexes **1** and **2**

V_a, ml (5.00×10^{-4} M)*	C_a°, $\times 10^{-4}$	Ratio (*a/d*)	*A*				$C_d^\circ + C_a^\circ$, $\times 10^{-4}$	$C_d^\circ . C_a^\circ$, $\times 10^{-8}$	$C_d^\circ . C_a^\circ / A$, $\times 10^{-8}$			
			1, 354 nm	**1**, 400 nm	**2**, 845 nm	**2**, 743 nm			**1**, 354 nm	**1**, 400 nm	**2**, 845 nm	**2**, 743 nm
0.25	0.25	0.25	0.601	0.550	0.198	0.065	1.25	0.25	0.42	0.45	1.26	3.85
0.50	0.50	0.50	0.788	0.954	0.381	0.125	1.50	0.50	0.63	0.52	1.31	4.00
0.75	0.75	0.75	0.845	1.432	0.525	0.190	1.75	0.75	0.89	0.52	1.43	3.95
1.00	1.00	1.00	0.861	1.525	0.682	0.250	2.00	1.00	1.16	0.66	1.47	4.00
1.25	1.25	1.25	0.873	1.535	0.782	0.284	2.25	1.25	1.43	0.81	1.60	5.04
1.50	1.50	1.50	0.862	1.539	0.903	0.317	2.50	1.50	1.74	0.97	1.66	4.73
1.75	1.75	1.75	0.861	1.538	1.025	0.349	2.75	1.75	2.03	1.14	1.71	5.01
2.00	2.00	2.00	0.860	1.539	1.125	0.380	3.00	2.00	2.33	1.30	1.78	5.26
2.50	2.50	2.50	0.855	1.541	1.364	0.454	3.50	2.50	2.92	1.62	1.83	5.51
3.00	3.00	3.00	0.850	1.544	1.582	0.510	4.00	3.00	3.53	1.94	1.90	5.88

*V_d, is 1 ml (5.00×10^{-4} M); C_d° is 1.00×10^{-4} M in all systems.

Table 3.
Spectrophotometric results for HPyO CT-complexes in EtOH

complex	λ_{max} (nm)	K_C ($l \cdot mol^{-1}$)	ε_{max} ($l \cdot mol^{-1} \cdot cm^{-1}$)	E_{CT} (eV)	f	μ	I_p (ev)	ΔG_o (25°C) ($K \cdot J \cdot mol^{-1}$)
[(H_2PyO)(PA)]	354 400	-1.04×10^4 -1.43×10^4	0.87×10^4 1.76×10^4	3.51 3.11	17.28 15.20	36.22 35.95	10.04 15.32	-2.29×10^4 -2.37×10^4
[(PyO)(HTCNQ)]	743 845	0.29×10^4 0.25×10^4	1.26×10^4 4.10×10^4	1.67 1.47	11.37 40.55	42.18 85.45	7.75 7.57	-1.98×10^4 -1.94×10^4

Table 4.

Characteristic infrared frequencies* (cm^{-1}) and tentative assignments for complexes **1** and **2**

HPA	TCNQ	HPyO	1	2	Assignments
3433 sh, br	3428 wbr	3436, br, m	3399 br, m		ν(O-H); H bonded
3101 s	3137 w	3119, m	3100, sh	3100, m	ν(N-H)
	3050 s	3072, m	3047, m	3069 m, br	
2976 sh	2969 w	2921,m	2960, w	2985 m	ν_s(C-H)
2873 w	2928 w	2815, m		2872 m	ν_{as}(C-H)
	2851 w			2467, w	
		2366, w	2365, m	2366, w	Hydrogen bonding
1851 w					$\nu(NO_2)$
	2222 vs				ν(C≡N); TCNQ
	1994 w			2252 w	
		1682, s		1850 w	ν(C=O)
		1641, sh			
	1671 w	1531, m		1646 vs	ν(C=N)
		1459, m		1573 vs	ν(C=C)
			1659, s		ring breathing bands
1640 vs	1542 vs				
1607 vs			1535 s		$\nu_{as}(NO_2)$, PA
1559 sh			1467 w		
1429 s					C-H deformation
1347 vs			1426 w		$\nu_s(NO_2)$; PA
1316 m			1342 m,br		
1267 s	1352 m	1425, m		1422 s	C-H deformation
1183 w	1285 vw	1364, sh		1237 s	ν(C-C)
1147 s	1205 vw	1250, w	1115 m		ν(C-N)
1083 s	1132 w	1144, w			ν(C-O)
	1045 vw	1101, w		1150 m	
		1030, vw		1092 m	
942 w	997 vw	986, m	997 m	979 s	
915 s	960 vw	919, m		920 m	C-H bend
826 w			861 s		δ(ONO); PA
783 s	861 vs	866, m	775 w	776 s	
733 vs	808 w	769, s	688 w	724 m	Skeletal vibration,
698 vs	622 vw	720, m		610 w	
646 sh		609, m		552 m	ν(C-O-C)
		575, vw		519 m	
		510, m			
550 m					CNC def.
530 m					CH out of plan bend,
448 vw	496 w				skeletal vibration
	474 s	432, w	479 m	470 m	(ONO); PA

*: s, strong; w, weak; m, medium; sh, shoulder; v, very; br, broad.

Table 5.
^{1}H NMR δvalues (ppm) of reactants and CT-complexes in dmso-d_6

Complex	H_3	H_4	H_5	H_6	N_1-H O_2-H	$H_{2,3}/H_{5,6}$ (TCNQ)	N^+-H	H_3/H_5 (HPA)	OH
HPyO	6.48, dd	6.99, m	5.79, m	7.29,d	8.02, s				
HPA								8.57, s	11.94*
TCNQ						9.06, s			
(H_2PyO)Cl	6.81, dd	7.30, m	5.96, m	7.61, d	9.00, br		5.00, br		
[(H_2PyO)(PA)]	6.84, dd	7.32, m	5.98, m	7.65, d	9.11, br		5.00, br	8.55, s	
[(PyO)(HTCNQ)]	6.62, dd	7.25, m	5.86, m	7.45, d	Not observed	8.99, s	6.78, s		

* Observed in $CDCl_3$.

Table 6.
The maximum temperature values for the decomposition along with the species lost in each step of the decomposition reactions of complexes **1** and **2**

Complex	Decomposition	T_{max}/ °C	Lost species	% Weight loss	
				Found	Calc.
HPyO	First step (Total loss)	207	C_5H_5NO	99.86	100.00
	Residue		--	00.14	00.00
[(H_2PyO)(PA)] (**1**)	First step (Total loss)	237	$C_{11}H_8N_4O_8$	99.99	100.00
	Residue			00.01	00.00
[(PyO)(HTCNQ)] (**2**)	First step	137	C_5H_4NO	30.50	31.44
	Second step	265	$C_{12}H_5N_4$	68.50	68.56
	Total loss		$C_{17}H_9N_5O$	99.00	100.00
	Residue			01.00	00.00

Table 7.
Thermodynamics parameters of the decomposition of HPyO and its complexes (**1**, **2**)

Compound	*T* (K)	Δ*G*° (kJ/mol)	Δ*H*° (kJ/mol)	Δ*S*° (kJ/mol)	Linear regression coefficient (r)
HPyO	423	-28.4204	270.3194	462.4725	99
	473	-18.7405			
	493	-13.3609			
1	425	-24.902	172.9944	269.3696	99
	473	-21.0742			
	510	-14.2433			
2	423	-29.8824	172.2668	231.8773	99
	473	-25.9452			
	523	-19.1517			

Table 8.

Antibacterial activity of HPyO and its complexes

Antibacterial activity (inhibition zone diameter in mm)				
Compounds	Bacteria			
	Bacillus subtillis, G^+	*Staphylococcus aureus*, G^+	*Esherichia. Coli, G*−	*Pseudomonas aeroginosa*, G−
HPyO	9	6	8	7
[(H_2PyO)(PA)] (**1**)	17.0	18.0	14.0	13.0
[(PyO)(HTCNQ)] (**2**)	12.0	07.0	13.0	11.0
DMSO	00.0	00.0	00.0	00.0
Ampicilin	25.0	26.0	25.0	24.0

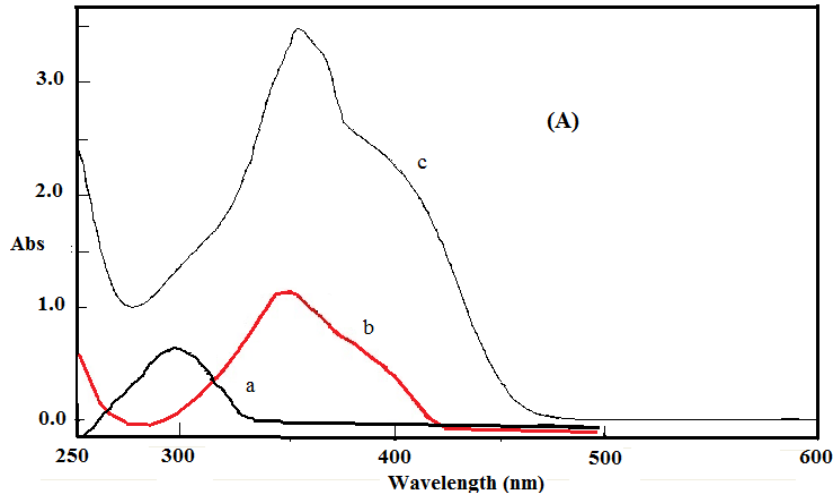


Fig.1A. Electronic absorption spectra of HPyO–HPA reaction (a: [HPyO] = 1.0×10^{-4} M, b: [HPA] = 1.0×10^{-4} M and c: HPyO–HPA product = 1.0×10^{-4} M) in EtOH.

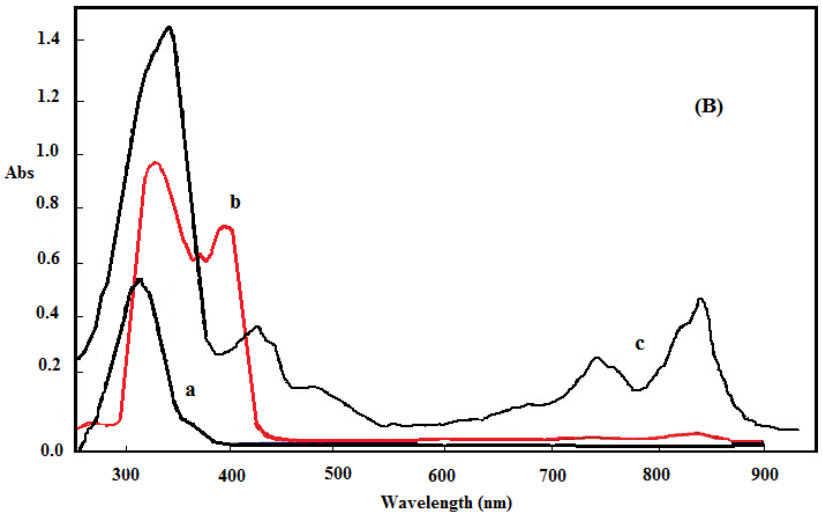


Fig.1B. Electronic absorption spectra of HPyO –TCNQ reaction (a: [HPyO] = 1.0×10^{-4} M, b: [TCNQ] = 1.0×10^{-4} M and c: HPyO–TCNQ product = 1.0×10^{-4} M) in EtOH.

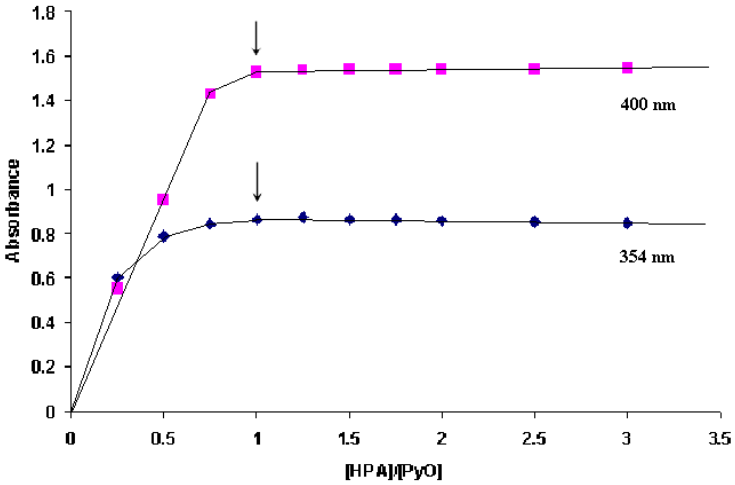


Fig. 2A. Photometric titration curves of HPyO–HPA reaction in EtOH at 354 and 400 nm.

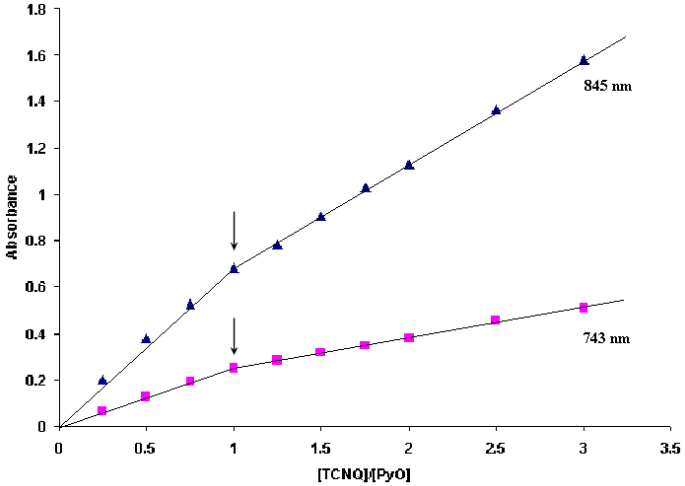


Fig. 2B. Photometric titration curves of HPyO–TCNQ reaction in EtOH at 743 and 845 nm.

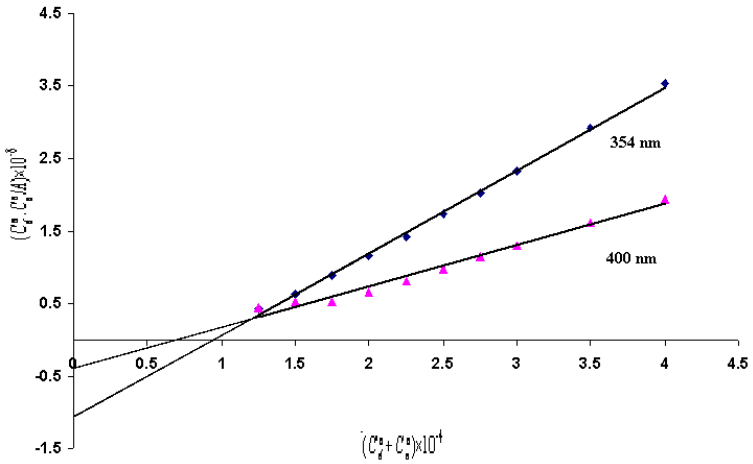


Fig. 3A. Relation between $C_d^\circ . C_a^\circ /A$ and $C_d^\circ + C_a^\circ$ for: (A) HPyO–HPA system in EtOH at 354 and 400 nm.

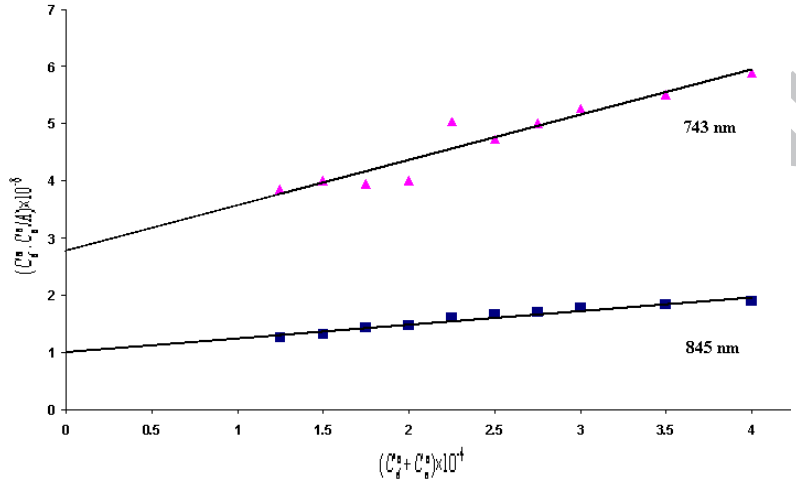
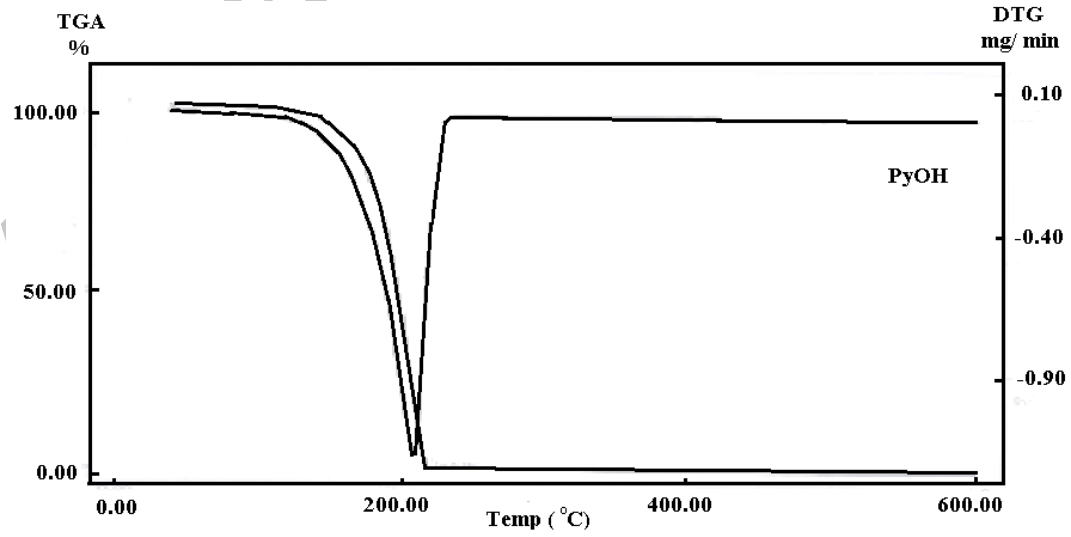


Fig. 3B. Relation between $C_d^\circ . C_a^\circ /A$ and ($C_d^\circ + C_a^\circ$) for: (A) HPyO–TCNQ system in EtOH at 845 nm and 743 nm.



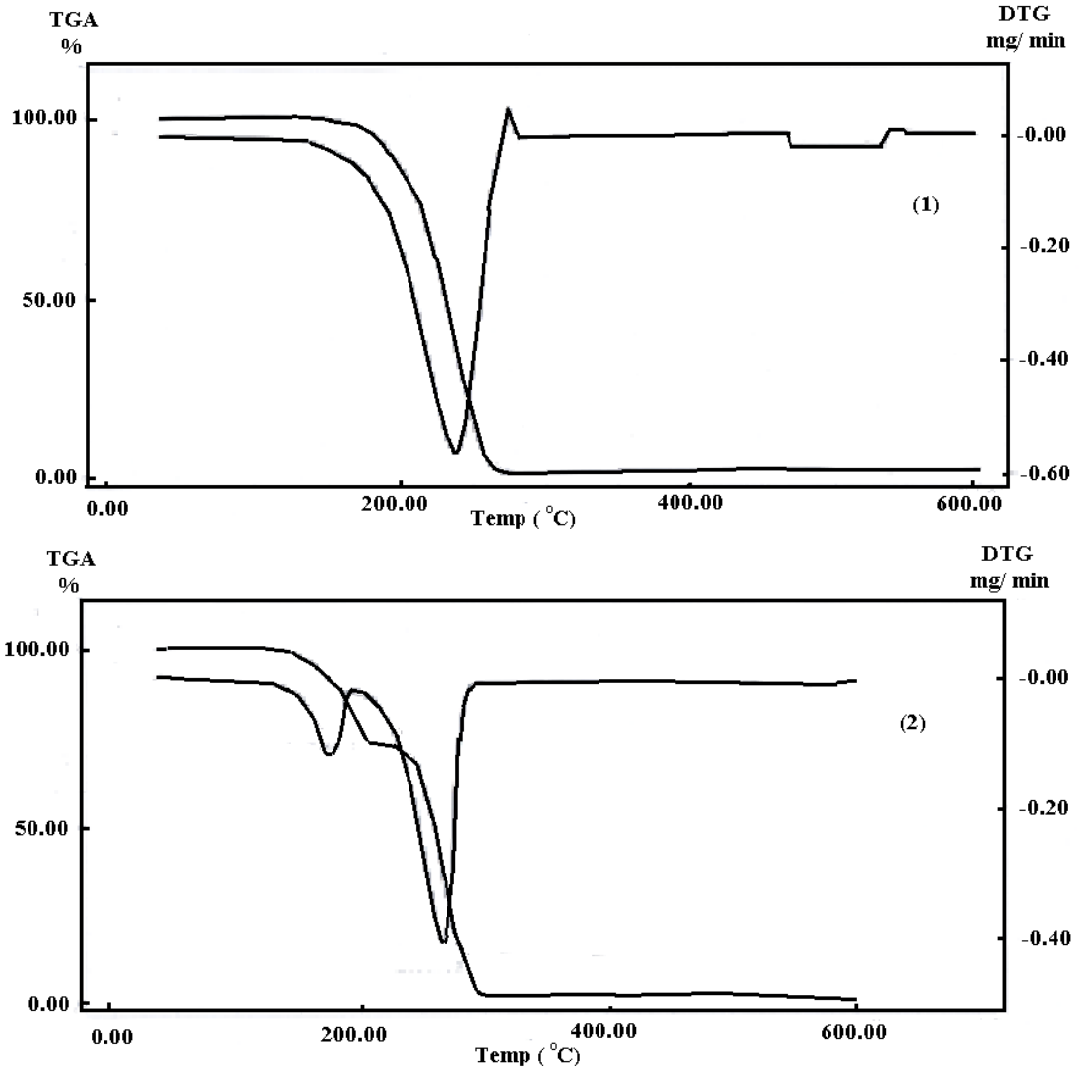
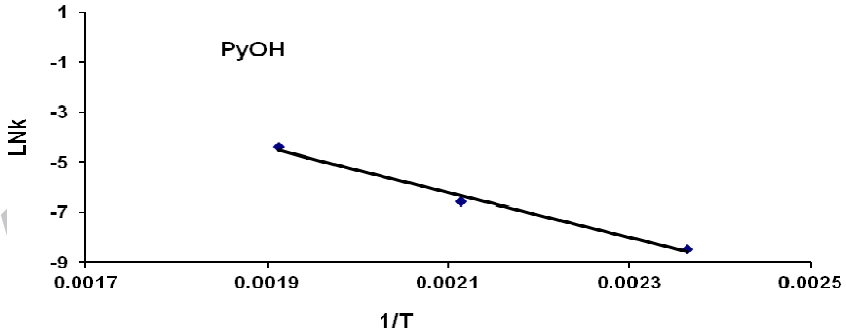


Fig. 4. Thermogravimeteric (TGA) and derivative (DTG) of HPyO and its complexes **1**and **2**



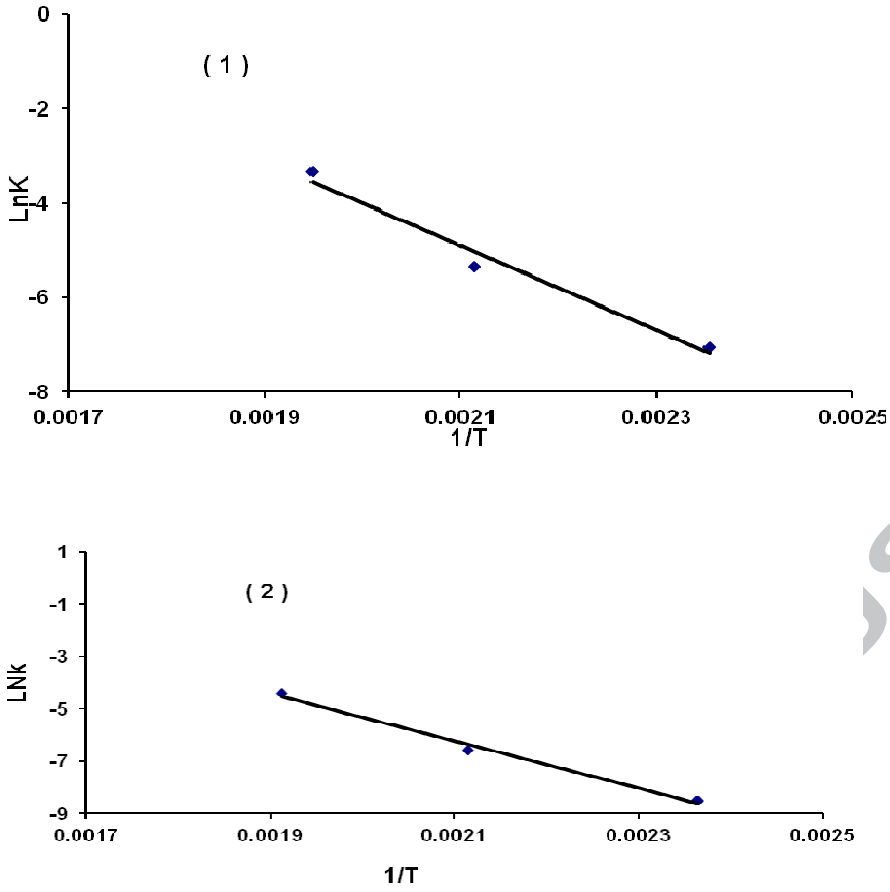
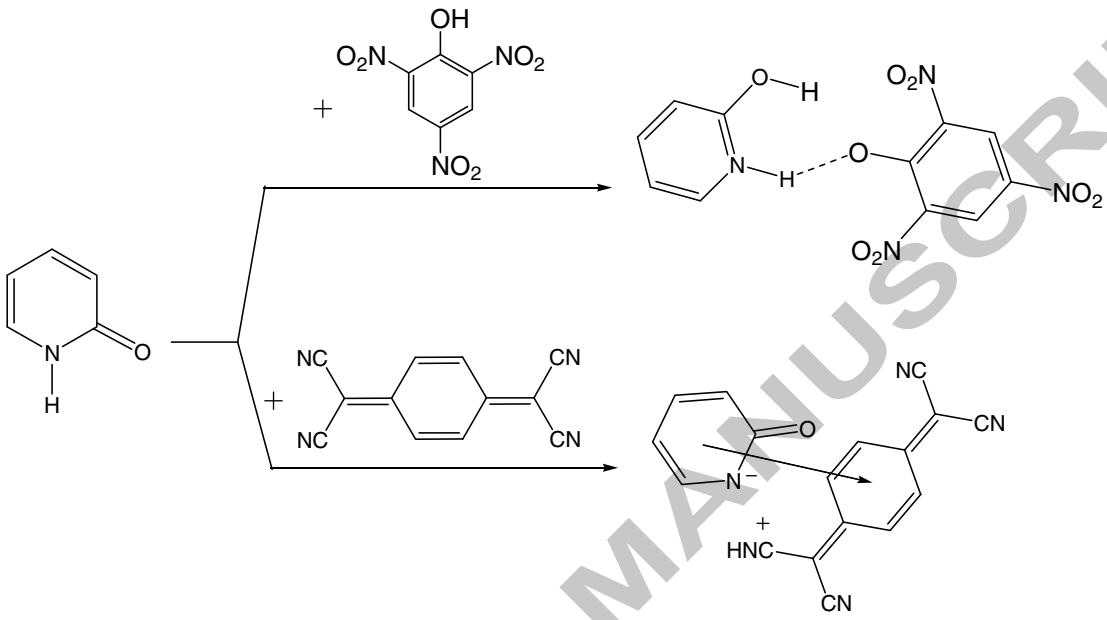


Fig. 5. Thermodynamics parameters of the decomposition of HPyO and its complexes **1** and **2**

Graphical abstract:

Preparation, spectroscopic and antibacterial studies on charge-transfer complexes of 2-hydroxypyridine with picric acid and 7,7`,8,8`-tetracyano-*p*-quinodimethane



Highlights

- Spectroscopic investigations on the interaction of 2-hydroxypyridine as an electron donor with electron acceptors.
- Electron acceptors used in this study are picric acid (HPA) and 7,7`,8,8`-tetracyano-*p*-quinodimethane (TCNQ) .
- The prepared CT-complexes have the general formulas [(H_2PyO)(PA)] and [(HPyO)(TCNQ)].
- The CT-complexes are characterized through elemental and thermal analyses, UV-Vis, IR, ^{1}H NMR spectroscopies.
- The values of K_C, E_{CT}, f, μ, I_p ΔG_o, and antimicrobial data of CT-complexes are presented.