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Spectroscopic and physical measurements on charge-transfer complexes: Interactions between norfloxacin and ciprofloxacin drugs with picric acid and 3,5-dinitrobenzoic acid acceptors

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ABSTRACT

Charge-transfer complexes formed between norfloxacin (nor) or ciprofloxacin (cip) drugs as donors with picric acid (PA) and/or 3,5-dinitrobenzoic acid (DNB) as π-acceptors have been studied spectrophotometrically in methanol solvent at room temperature. The results indicated the formation of CT-complexes with molar ratio1:1 between donor and acceptor at maximum CT-bands. In the terms of formation constant (K_{CT}), molar extinction coefficient (ε_{CT}), standard free energy (ΔG^{o}), oscillator strength (f), transition dipole moment (μ), resonance energy (R_N) and ionization potential (I_D) were estimated. IR, H NMR, UV–Vis techniques, elemental analyses (CHN) and TG–DTG investigations were used to characterize the structural of charge-transfer complexes. It indicates that the CT interaction was associated with a proton migration from each acceptor to nor or cip donors which followed by appearing intermolecular hydrogen bond. In addition, X-ray investigation was carried out to scrutinize the crystal structure of the resulted CT-complexes.

1. Introduction

Charge-transfer complexes were known to take part in many chemical reactions like addition, substitution and condensation [1,2]. These complexes have great attention for non-linear optical materials and electrical conductivities [3–6]. Electron donor–acceptor (EDA) interaction is also important in the field of drug–receptor binding mechanism [7], in solar energy storage [8] and in surface chemistry [9] as well as in many biological fields [10]. On the other hand, the EDA reactions of certain π-acceptors have successfully been utilized in pharmaceutical analysis [11]. For such wide applications extensive studies on CT-complexes of π-acceptors have been performed [12]. Charge-transfer complexes of organic species are intensively studied because of their special type of interaction, which is accompanied by transfer of an electron from the donor to the acceptor [13,14]. Also, protonation of the donor from acidic acceptors are generally root for the formation of ion pair adducts [15–17].

Ciprofloxacin and norfloxacin (Formula 1) are considerably a second generation class of a synthetic fluoroquinolone [18].

The charge-transfer reactions of (nor) and (cip) with picric acid and/or 3,5-dinitrobenzoic acid have not yet been reported in the literature, therefore the aim of our present study was directed to investigate these reactions. Results of the elemental analyses for the norfloxacin and ciprofloxacin charge-transfer complexes are listed in Table 1. From this table, it can be seen that the found values are in a good agreement with the calculated ones, and the composition of the CT-complexes are matched with the molar ratios presented from the photometric titration occurs between (nor) or (cip) and picric acid and/or 3,5-dinitrobenzoic acid acceptors. These complexes are insoluble in cold and hot water, but easily soluble in dimethyl formamide (DMF) and dimethylsulfoxide, d_6 (DMSO).

2. Experimental

Norfloxacin and ciprofloxacin were of analytical reagent grade (Merck reagent). The picric and 3,5-dinitrobenzoic acids acceptors were supplied from Aldrich. Stock solutions of norfloxacin, ciprofloxacin, picric acid or 3,5-dinitrobenzoic acid were freshly prepared and spectroscopic grade that used as received.

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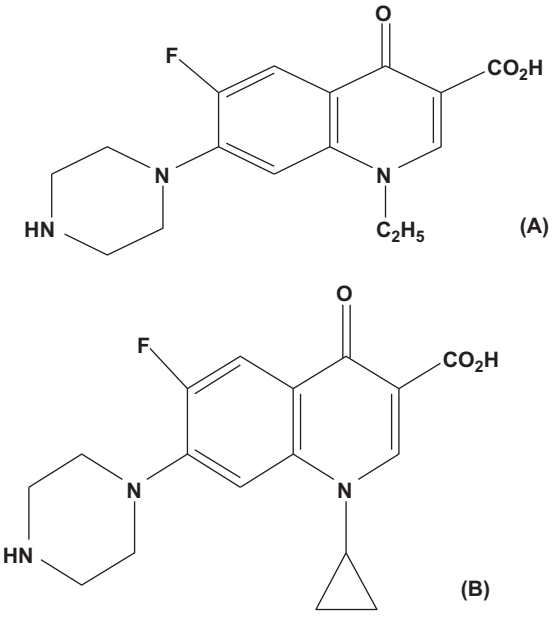


Formula 1. (A) Norfloxacin (nor) and (B) ciprofloxacin (cip).

2.1. Nor-PA and nor-DNB complexes

The solid CT-complexes of (nor) with acceptors (PA and DNB, Formula 2) were prepared by mixing 1 mmol of (nor) donor in 10 mL methanol with 1 mmol of each acceptor in the same solvent with stirring for about 6 h. The solutions were allowed to evaporate slowly at room temperature, the solids precipitates filtered off and washed several times with little amounts of the same solvent and dried under vacuum over anhydrous calcium chloride. The charge-transfer complexes: [(nor)(PA)] (yellow) formed with empirical formula as $C_{22}H_{21}FN_6O_{10}$ with molecular weight 548.40 g/mol and [(nor)(DNB)] (buff) formed with empirical formula as $C_{23}H_{22}FN_5O_9$ with molecular weight 531.42 g/mol.

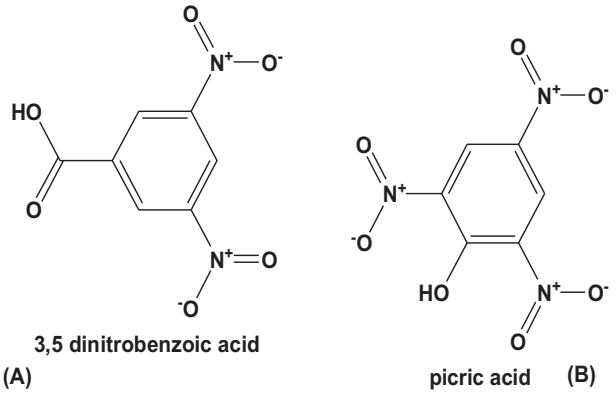
2.2. Preparation of cip-PA acid charge-transfer complex

The cip-PA CT complex with the general formula [(cip)(PA)] was isolated by mixing (0.331 g, 1.0 mmol) of (cip) donor in 10 mL methanol, a solution of PA was added (0.229 g, 1.0 mmol) in the same solvent with continuously stirring for about 5 h at room temperature and the solution was allowed to evaporate slowly at room temperature. A pale yellow powder was formed, washed several times with little amounts of methanol and dried under vacuum over anhydrous calcium chloride. The empirical formula of the [(cip)(PA)] complex is $C_{23}H_{21}FN_6O_{10}$ with molecular weight 560.45 g/mol.

2.3. Instrumentation and physical measurements

2.3.1. Crystal structure

Structural investigations were performed utilizing X-ray diffraction, PHILIPS X-Pert Diffractometer with Ni filter and Cu Kα radiation (λ = 1.5419).



Formula 2. Structures of: (A) 3,5-dinitrobenzoic acid and (B) picric acid.

2.3.2. Electronic spectra

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.

2.3.3. Infrared spectra

IR measurements (KBr discs) of the solid donors, acceptor and CT-complexes were carried out on a Bruker FT-IR spectrophotometer (400–4000 cm^{-1}).

2.3.4. ^1H NMR spectra

^1H NMR spectra were obtained on a Varian Gemini 200 MHz spectrometer. ^1H NMR data are expressed in parts per million (ppm), referenced internally to the residual proton impurity in DMSO solvent.

2.3.5. Thermal analysis

The thermal analyses TGA, and DTG were carried under nitrogen atmosphere with a heating rate of 10 °C/min using a Shimadzu TGA-50H thermal analyzers.

3. Results and discussion

3.1. X-ray examination

For investigating the crystal structure of the obtained complexes; samples in powder form were X-ray examined, the diffraction patterns were displayed. According to the obtained patterns, the samples were in a polycrystalline form. CMPR program has been applied to index the diffraction pattern of the investigated materials [19], since there are no available structural data. It has been recognized that the structure of nor/PA, cip/PA and nor/DNB systems are well designated by monoclinic system. In Table 2, the corresponding lattice parameters, volume and X-ray data of [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] CT-complexes are given where the volume is equal $a*b*c$ sin β [20].

Table 1
Elemental analysis CHN and physical parameters data of the [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] CT-complexes.

Complexes	Mwt	C%		H%		N%		Physical data	
		Found	Calc.	Found	Calc.	Found	Calc.	Λm (μs)	mp (°C)
[(nor)(PA)]	548.40	47.81	48.14	3.80	3.83	15.10	15.32	32	~300
[(cip)(PA)]	560.45	48.87	49.25	3.66	3.75	14.78	14.99	28	~300
[(nor)(DNB)]	531.42	51.38	51.94	4.02	4.14	13.08	13.17	31	~300

Table 2
The corresponding lattice parameters a, b, c, α, β, γ, volume v and X-ray data of the nor-PA, cip-PA and nor-DNB complexes.

Name of sample	System	a (Å)	b (Å)	c (Å)	α	β	γ	v (Å^3)	h	k	l	2θ	d-obs	d-calc
NOR-PA complex	Monoclinic	8.432763	6.24722	8.279976	90	100	90	429.52	0	1	0	6.51	6.25	6.272
									−1	1	1	9.118	4.471	4.421
									2	0	0	9.81	4.156	4.26
									−2	0	1	10.218	3.99	3.988
									2	1	1	13.471	3.029	3.043
									1	1	2	13.571	3.007	3.021
									1	2	0	13.964	2.923	2.925
									2	1	2	16.54	2.47	2.46
									0	1	3	20.28	2.018	2.012
									−1	1	3	20.67	1.98	1.971
									4	1	0	20.79	1.969	1.96
									4	0	1	21.172	1.9344	1.934
									1	3	2	23.03	1.7801	1.773
									−4	1	3	23.605	1.7364	1.737
									0	2	4	24.03	1.7078	1.707
									3	3	1	25.69	1.5977	1.598
									3	2	3	26.46	1.5518	1.553
									−5	2	1	27.7	1.481	1.483
									2	4	0	28.1	1.461	1.462
Cip-PA complex	Monoclinic	9.309277	9.014438	7.103755	90	91.1896	90	596	1	0	0	4.37	9.34	9.39
									0	1	1	4.519	9.012	9.012
									1	2	0	10.05	4.052	4.16
									−1	0	2	12.212	3.3416	3.347
									−2	2	1	13.78	2.965	2.958
									−3	1	1	14.95	2.730	2.727
Cip-PA complex	Monoclinic	9.309277	9.014438	7.103755	90	91.1896	90	596	2	2	2	17.26	2.376	2.373
									−3	0	2	17.31	2.306	2.358
									−4	0	1	18.393	2.2228	2.2218
									3	3	0	18. 97	2.156	2.1556
									4	1	1	19.168	2.1345	2.1335
									2	1	3	20.073	2.0391	2.0165
									4	3	0	22.253	1.8415	1.8374
									3	3	2	22.361	1.8323	1.8211
									−4	2	2	22.76	1.8010	1.799
									2	4	2	23.368	1.7547	1.754
									3	4	2	25.442	1.6138	1.6125
									−3	5	1	26.931	1.526	1.523
									3	1	4	27.297	1.5060	1.505
NOR-DNB complex	Monoclinic	11.186452	5.438887	10.621446	90	104.591026	90	625.39	0	1	0	7.48	5.446	5.62
									−1	0	2	7.849	5.172	5.175
									2	0	1	9.36	4.3553	4.418
									−2	0	2	9.49	4.305	4.398
									0	0	3	11.930	3.4178	3.536
									−4	0	2	15.169	2.692	2.688
									0	0	4	15.88	2.5713	2.573
									−3	0	4	17.04	2.3981	2.395
									1	0	4	17.25	2.369	2.377
									0	1	4	17.60	2.322	2.326
									−4	1	3	18.37	2.2261	2.224
									−5	0	2	18.55	2.2051	2.199
NOR-DNB complex		11.186452	5.438887	10.621446	90	104.591026	90	625.39	0	0	5	19.91	2.059	2.059
									−2	1	5	20.83	1.964	1.974
									−4	2	2	21.416	1.9118	1.93
									3	0	4	21.76	1.882	1.886
									5	1	2	23.57	1.739	1.743
									6	0	1	24.03	1.7055	1.706
									2	3	1	24.501	1.674	1.64
									−5	2	3	24.851	1.652	1.629

3.2. Microstructure analysis

The calculation of the crystallite size of nor/PA, cip/PA and nor/DNB complexes were performed by using simulation program [21]. Fig. 1 represents the output of the winfit program from which the crystallite size was deduced to be 2258 Å, 1302 Å and 2260 Å, respectively, for nor/PA, cip/PA and nor/DNB.

3.3. Electronic absorption spectra of nor/PA, cip/PA and nor/DNB system

The electronic absorption spectra of nor/PA, cip/PA and nor/DNB systems were measured in MeOH solvent. In case of MeOH solvent the complexes were formed by adding X ml of 5.0×10^{-4} M (acceptor = PA and/or DNB) (X = 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50 and 3.00 ml) to 1.00 ml of 5.0×10^{-4} M of nor and/or cip as donors. The volume of the mixtures in each case was completed to 10 ml with the respected solvent. In the reaction mixture the concentration of (nor and/or cip) was kept fixed at 0.50×10^{-4} M in the MeOH solvent, while, the concentration of PA and/or DNB was varied over the range of $0.125–1.500 \times 10^{-4}$ M. These concentrations produce donor: acceptor ratios extending along the range from 1:0.25 to 1:3.00. Spectra of the electronic absorption of the 1:1 ratio in MeOH together with the reactants donors (nor and cip) and acceptors (PA and DNB) are shown in Fig. 2.

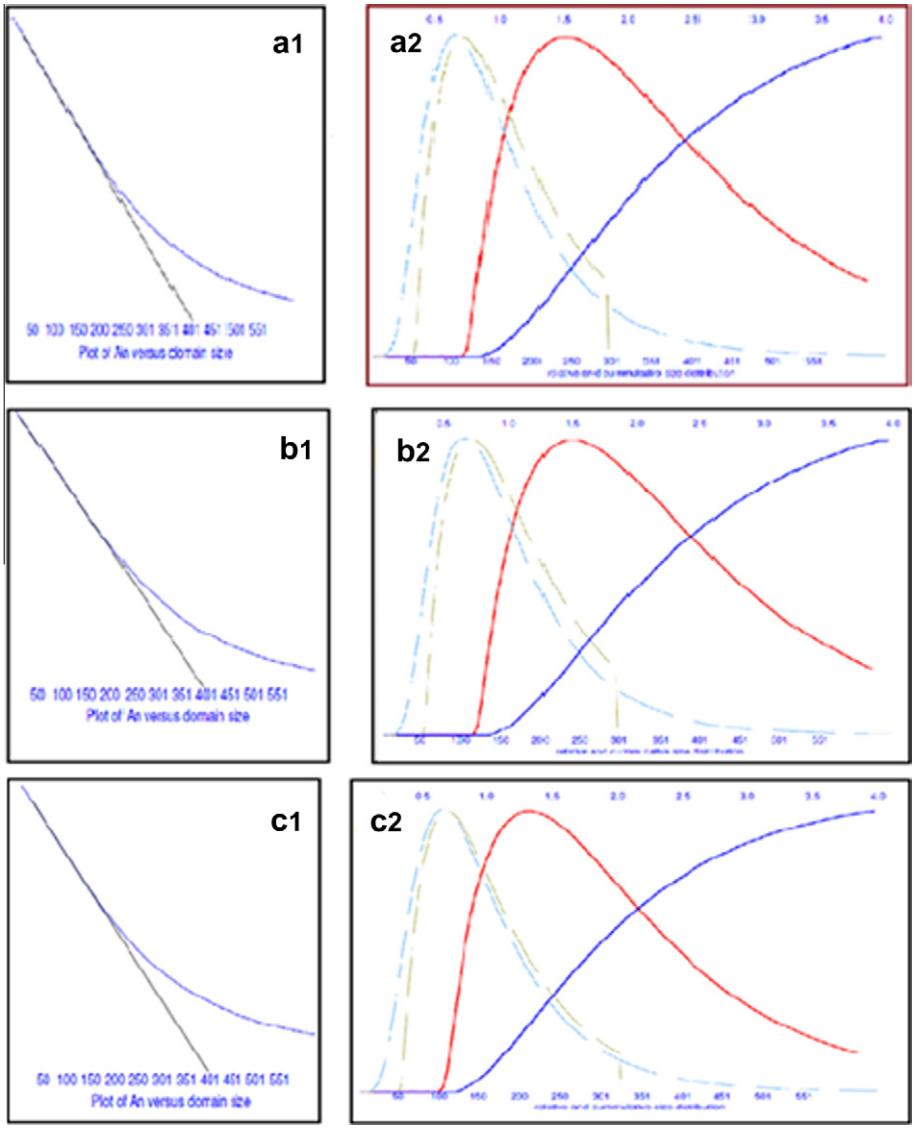


Fig. 1. The output of the winfit program of (a) [(Nor)(PA)], (b) [(Cip)(PA)] and (c) [(Nor)(DNB)] complexes.

The new characteristic absorption bands, which are not present in the spectra of the reactants free acceptors (PA and DNB) and donors (nor and cip), were refereed in the spectra. These bands at about 300, 278 and 297 nm are assigned to be due to the [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] CT-complexes formed charge transfer interactions. Photometric titration curves based on these characterized absorption bands are given in Fig. 3. The photometric titration curves were obtained according to the well known methods by plotting of the absorbance against the X ml added of the PA and/or DNB as π-acceptors [22]. In these curves the equivalent points clearly indicate that the formed CT-complexes between (nor and/or cip) and (PA and/or DNB) are 1:1. The formation of 1:1 complexes were strongly supported by elemental analysis, mid infrared, ^{1}H NMR, and thermal analysis TG/DTG. Calculations, based upon the modified Benesi–Hildebrand (1:1) equation, were executed for [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] CT-complexes as follow [23].

$$\frac{C_a^o C_d^o l}{A} = \frac{1}{K\varepsilon} + \frac{C_a^o + C_d^o}{\varepsilon}. \quad (1)$$

where C_a^o and C_d^o are the initial concentrations of the acceptors and the donors, respectively. l is a path length and A is the absorbance of the detected bands at 300, 278 and 297 nm due to the [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] CT-complexes. In Eq. (1), K and ε represent the equilibrium constant and extinction coefficient respectively. When the $C_a^o \cdot C_d^o/A$ values for each system are plotted against the corresponding $(C_a^o + C_d^o)$ values straight lines were obtained with a slope of $1/\varepsilon$ and intercept of $1/K\varepsilon$ as shown in Fig. 4 for the reactions in MeOH. The oscillator strength f was obtained from the approximate formula [24].

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

where $\nu_{1/2}$ is the band-width at half-intensity in cm^{-1}. The oscillator strength values together with the corresponding dielectric constants, D, of the solvent used are given in Table 3. Regarding Table 3, several facts may be considered. The CT-complexes of nor and cip have a high values of both K and ε. Such high value of (K) reflects the high stability of nor and cip complexes as a result of the expected high donation of nor and cip.

The transition dipole moments (μ) of nor and cip CT-complexes, Table 3, have been calculated from the following equation [25]:

$$\mu = 0.0958[\varepsilon_{max}\nu_{1/2}/\nu_{max}]^{1/2} \ldots \quad (3)$$

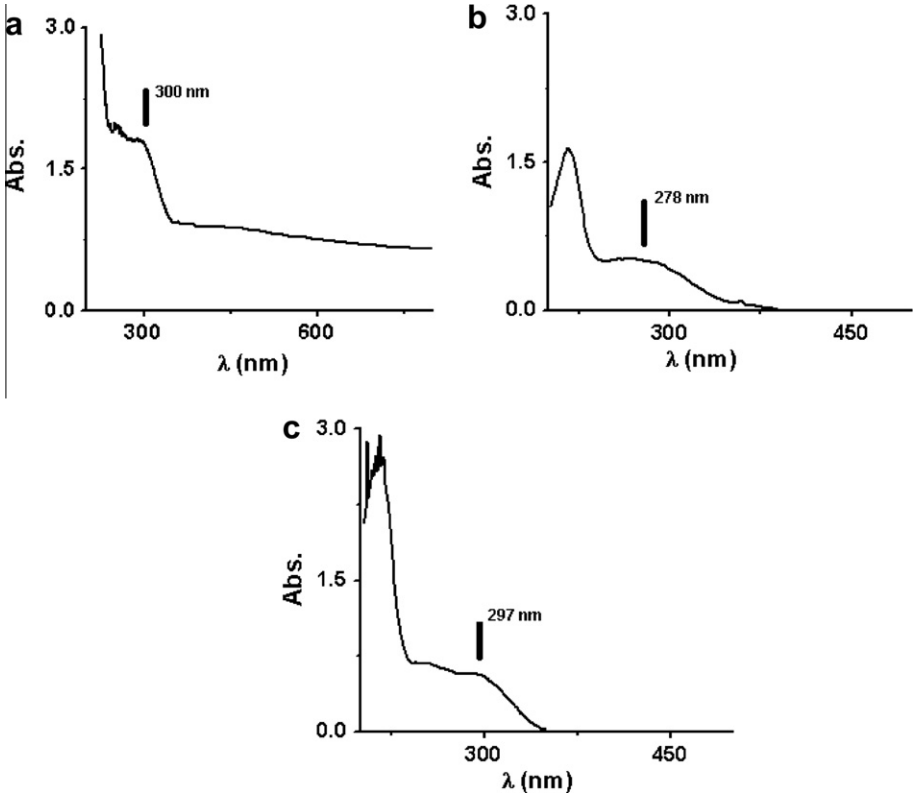


Fig. 2. Spectra of electronic absorption of: (a) nor-PA, (b) cip-PA and (c) nor-DNB reactions in MeOH.

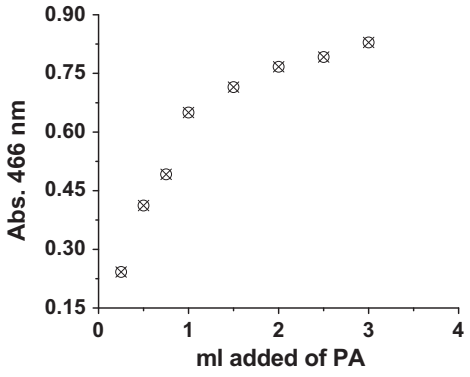


Fig. 3a. Photometric titration curve for the nor-PA system in MeOH at 300 nm.

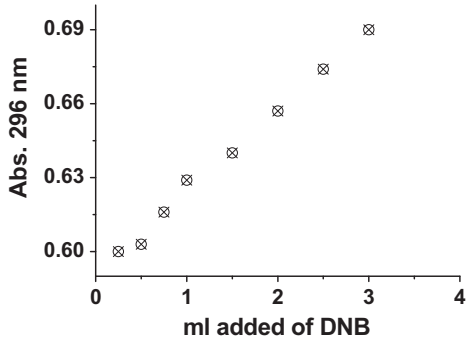


Fig. 3c. Photometric titration curve for the nor-DNB system in MeOH at 297 nm.

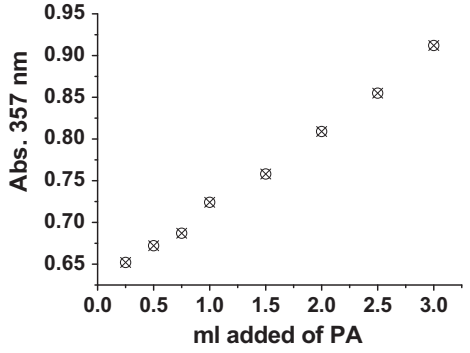


Fig. 3b. Photometric titration curve for the cip-PA system in MeOH at 278 nm.

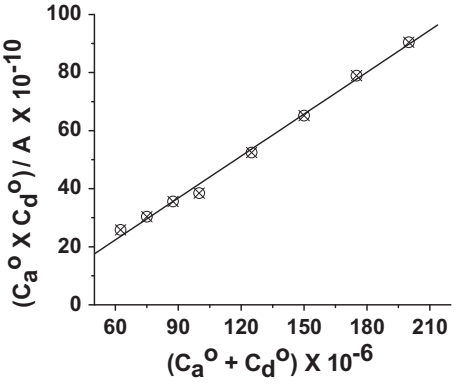


Fig. 4a. The plot of $(C_d^o + C_a^o)$ values against $(C_d^o \cdot C_a^o/A)$ values for the nor-PA system in MeOH at 300 nm.

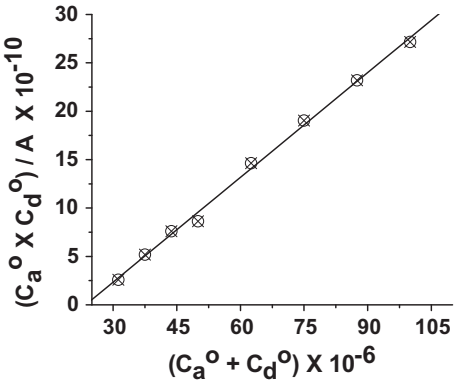


Fig. 4b. The plot of $(C_d^o + C_a^o)$ values against $(C_d^o \cdot C_a^o/A)$ values for the cip-PA system in MeOH at 278 nm.

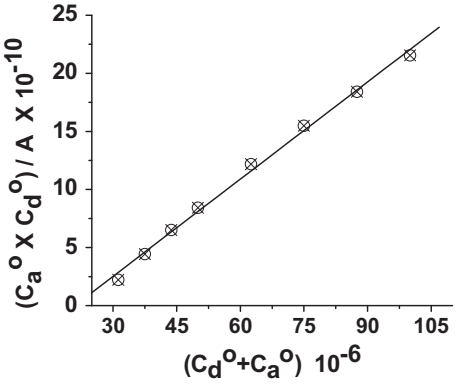


Fig. 4c. The plot of $(C_d^o + C_a^o)$ values against $(C_d^o \cdot C_a^o/A)$ values for the nor-DNB system in MeOH at 297 nm.

The ionization potential (I_p) of the free (nor and cip) donors were determined according to the CT band of complexes using the following relationship [26,27]:

$$I_p(eV) = 5.76 + 1.53 \times 10^{-4} v_{CT} \quad (4)$$

The energy of the charge-transfer E_{CT} of the [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] CT-complexes were calculated using the following equation [25]:

$$E_{CT} = (hv_{CT}) = 1243.667/\lambda_{CT}\ (\text{nm}) \quad (5)$$

The molar extinction coefficient of the complexes at the maximum of the CT absorption (ε_{max}) can be calculated as follows [19];

$$\varepsilon_{max} = 7.7 \times 10^{-4}/[hv_{CT}/[R_N] - 3.5] \quad (6)$$

where λ_{CT} is the wavelength of the complexation band, R_N is the resonance energy (R_N), v_{CT} is the frequency of the CT peak and R_N is the resonance energy of the complexes in the ground state, which, obviously is a contributing factor to the stability constant of the complexes (a ground state property). The values of R_N for the [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] of the studied complexes were reported in Table 3. The standard free energy change of complexation (ΔG^o) was calculated from the association constants by the following equation [19].

$$\Delta G^o = -2.303RT\ \log K_{CT} \ldots \quad (7)$$

where ΔG^o is the free energy change of the complexes (kJ mol^{-1}), R is the gas constant (8.314 J mol^{-1} K), T is the temperature in Kelvin and K_{CT} is the association constant of the complexes (l mol^{-1}) in respective solvent at room temperature. The calculated values are represented in Table 3.

3.4. Infrared spectra

3.4.1. [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] CT-complexes

The infrared spectra of the free donors (nor and cip) and acceptors (PA and DNB) as well as the formed CT complexes [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] were discussed and their band assignments were reported in Table 4. The presence of a new IR spectral bands in the spectra of CT-complexes are confirmed the conclusion that a deformation of the electronic environment of nor and cip occurred by accepting proton from PA or DNB. The IR spectra of the three CT-complexes of PA and DNB were characterized by the presence of detected new bands in the region ~2300 to ~2800 cm^{-1}, which are absent in the spectra of the free donors and acceptors. These bands are attributed to the stretching vibrations of a hydrogen bonding [28]. These bands build up according to the protonation of the $^+$NH of the piperazine group of nor and cip donors *via* the transfer of one protons from the acidic center of PA and DNB acceptors to the basic center on the donor $^+$NH group. Therefore an intermolecular hydrogen bond occurs, in PA or DNB acceptor, between the OH group and the basic center nitrogen atom in case of nor or cip. Such assumption is strongly supported by the existence of an absorbance bands at (1622 and 1557 cm^{-1}), (1620 and 1562 cm^{-1}) and (1618 and 1531 cm^{-1}) for [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] complexes, respectively, due to $^+NH_2$ deformation and all absorbed bands ~800 cm^{-1} are attributed to NH_2 rock. The formation of $^+NH_2$ is also supported by disappear or decrease in the stretching vibrations of OH and COOH groups for PA and DNB, respectively.

The complexes [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] are slightly soluble in CH_3OH. The molar conductance values at 1.0×10^{-3} concentration indicated that these complexes have a small limit of conductivity. The data of conductivity confirms that these complexes have a positive charge ($^+NH_2$) and negative charge (O^- of acidic in PA and DNB) resulted from CT transition. The low conductivity values for the three CT-complexes may be due to intermolecular hydrogen bond formation.

Accordingly, the hydrogen bonding between the donors and the acceptors can be formulated as: (see Formula 3–5).

Table 3
Spectrophotometric results in MeOH solvent at 25 °C.

λ_{max} (nm)	E_{CT} (eV)	K (l mol^{-1})	ε_{max} (l mol^{-1} cm^{-1})	$f * 10^3$	$\mu * 10^3$	I_p	D	R_N	ΔG^o (25 °C) kJ mol^{-1}
[(nor)(PA)]									
300	4.14	12.00×10^4	0.50×10^4	2.00	13.00	9.04	33	0.141	28,981
[(cip)(PA)]									
278	4.47	5.00×10^4	3.60×10^4	21.00	38.00	10.04	33	0.617	26,812
[(nor)(DNB)]									
297	4.19	4.00×10^4	2.80×10^4	12.00	32.00	10.93	33	0.672	26,259

Table 4
Infrared frequencies[a] (cm^{-1}) and tentative assignments for [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] complexes.

[(nor)(PA)]	[(cip)(PA)]	[(nor)(DNB)]	Assignments
3471 vw	3861 vw,br	3744 vw	ν(N—H) + ν(O—H)
3442 w,br	3741 vw 3437 w,br	3423 s,br	
3200 vw	3147 vw	3088 vw	ν(C—H) hydrogen bond
3184 w	3062 w,br	3052 ms	
3072 m	2926 w	2972 m	
2976 vw	2835 w	2927 vw	
2844 w	2752 w	2835 m	
2762 w	2485 m	2715 w,br	
2718 w	2361 ms	2472 m	
2471 m		2368 vw	
2363 m			
1721 vs	1698 s	1718 vs	ν(C=O): (COOH)
1622 vs	1620 vs	1618 vs	ν(C=O) + $\delta_b(H_2O)$ + δ_{def}(N—H); $^+NH_2$
1557 s	1562 m	1531 s	Phenyl breathing modes
1476 vs	1500 vs	1488 s	CH; deformation of —CH_2—
1325 s	1392 w		
1319 s	1346 vs	$\delta_b(CH_2)$	
1262 s	1262 vs	1263 s	
1210 vw	ν(C—C)		
1169 vw	1160 w	1077 s	ν(C—O) + ν(C—N) + ν(C—C) + $\delta_r(CH_2)$
1089 w	1073 w	1028 w	
1026 mw	1030 m		
932 w	961 vw	929 s	CH-bend; phenyl
897 vw	939 vw	831 vw	δ_{rock}; $^+NH_2$
857 vw	895 m	819 vw	
813 w	830 vw	805 vw	
797 w	815 vw 796 vw		
749 ms	780 vw	722 vs	$\delta_b(COO^-)$
702 s	746 vw 702 ms		
557 m	545 w	563 ms	Ring deformation
510 m	471 vw	521 ms	δ(ONO); PA
451 vw	431 w	466 vw 425 vw	CNC deformation

ν, stretching; δ, bending.
[a] s = strong, w = weak, m = medium, sh = shoulder, v = very, br = broad;

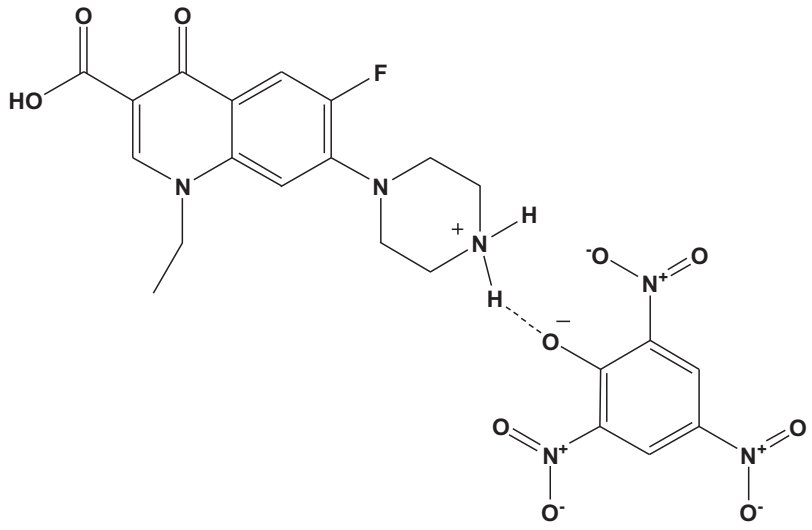
3.5. ^{1}H NMR spectra of [(nor)(PA)], [(cip)(PA)] and [(nor)DNB)] CT-complexes

^{1}H NMR spectra of (nor and cip) as free donors, (PA and DNB) as a free acceptors and [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] complexes in DMSO at room temperature were measured. The chemical shifts (ppm) of proton NMR for the detected peaks are assigned and listed in Table 5. The results obtained from elemental analysis and photometric titrations designate the same way with ^{1}H NMR spectra to suggest the mode of interaction between donor and acceptor as follows:

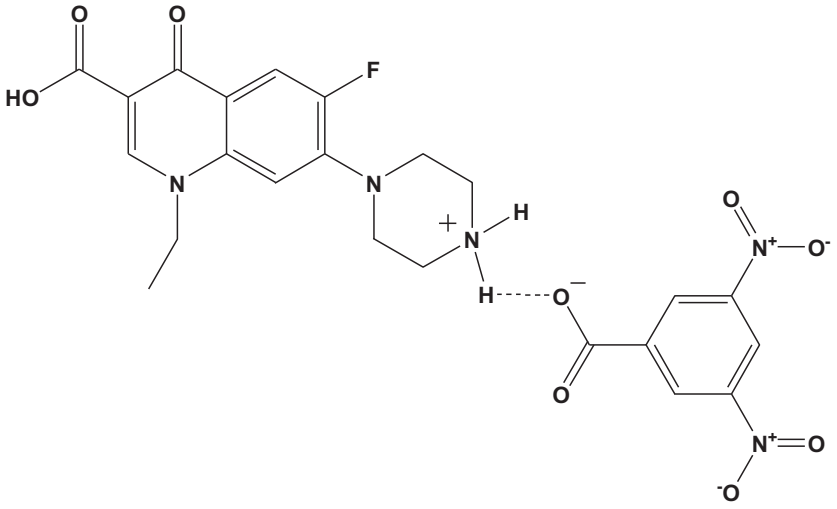
i. In case of [(nor)(PA)] and [(cip)(PA)] CT-complexes, the signal distinguishing proton of OH of PA acceptor at 8.90 ppm was disappeared due to deprotonation from acceptor-to-donor. Besides, the formation of new signals at 4.611 and 3.883 ppm for [(nor)(PA)] and [(cip)(PA)] CT-complexes, respectively, due to the presence of $^+NH_2$. The located of signals at 15.274 ppm for [(nor)(PA)] and at 15.190 ppm for [(cip)(PA)] were assigned to the proton of carboxylic group of nor and cip, which confirms the non participation of COOH in the complexation process.
ii. The mode of chelation concerning [(nor)(DNB)] complex was sustained by the presence of signal at 4.60 ppm due to the formation of $^+NH_2$ and absence of signal at 13.600 ppm was assigned to proton of COOH. These results match to each other according to the sharing of proton of carboxylic group of (DNB) acceptor with NH of piperazine ring (cip, donor).

3.6. Thermal analysis studies

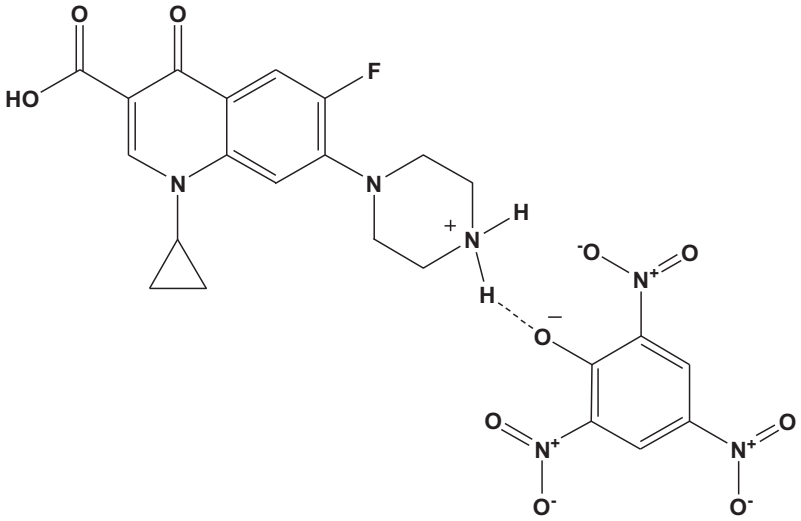
The [(nor)(PA)] complex starts to decompose at ~290 °C with simultaneous decomposition. The TG/DTG profile of this complex is shown in Fig. 5a. From TG curve, it appears that the sample decomposes in two stages over the range 290–800 °C. The first decomposition occurs between 284 and 304 °C with a mass loss of 42.43% while the second decomposition starts at 305 °C and ends at 800 °C with a 49.10% mass loss. Both decomposition stages (which may be attributed to the loss of $C_{18}H_{21}FN_6O_{10}$), is in reasonable agreement with the theoretical value of 91.25% over the whole range of temperature.



Formula 3. Structure of [(nor)(PA)] CT-complexes.



Formula 4. Structure of [(nor)(DNB)] CT-complexes.



Formula 5. Structure of [(cip)(PA)] CT-complexes.

Table 5
^{1}H NMR spectral data of free nor, [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] complexes.

nor	[(nor)(PA)]	[(cip)(PA)]	[(nor)(DNB)]	Assignments
1.13	1.442, 1.563	1.334	1.408	δ H, —CH_3
2.0	–	–	–	δ H, —NH; piperazine
2.78, 3.10, 3.47	2.665, 3.433, 4.611	2.602, 2.665	2.670, 3.442, 3.549, 4.600	δ H, —CH_2; piperazine δ H, —CH_2; —CH_2CH_3
		3.412, 3.493, 3.673, 3.883		$^{+}NH_2$
5.93, 7.12, 8.01	7.239, 7.869, 8.587, 8.956	7.461, 7.622, 7.973, 8.586, 8.685, 8.857	7.237, 7.847, 7.913, 8.800, 8.877, 8.923	δ H, —CH aromatic
15.00	15.274	15.215	–	δ H, —COOH

Regarding Fig. 5b, [(nor)(DNB)] CT-complex thermally decomposes in three successive steps within the temperature rang 25–800 °C. The decomposition steps started clearly at 300 °C with experimental weight loss of 14.25%, 28.39%, and 53.24%, respectively, were attributed to the loss of $C_{21}H_{22}FN_5O_9$ organic moiety with a final residual carbon.

As indicated in Fig. 5c, the charge transfer of [(cip)(PA)] complex decomposes in two stages with a sharp differential thermogravimetric analysis at 305 °C. The first stage ranges from 284 till 314 °C with a weight loss 44.50% and the second stage extend to 800 °C with 53.89% weight loss.

3.7. Kinetic studies

Two major different methods were applied for the evaluation of kinetic parameters as follow:

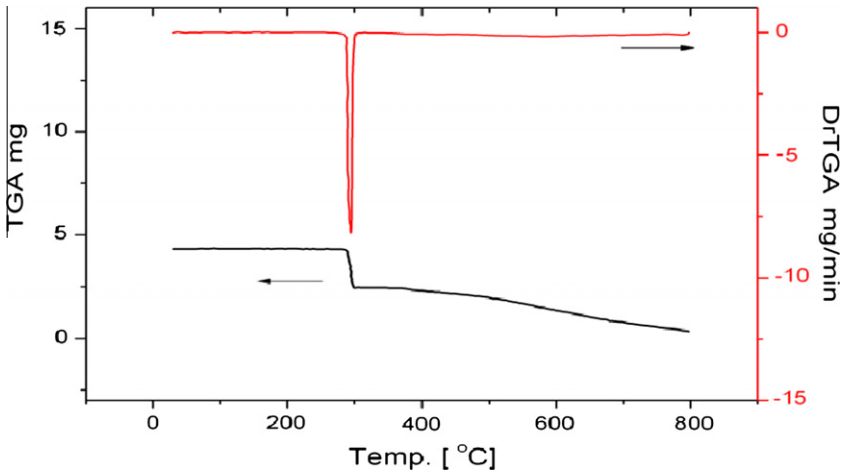


Fig. 5a. TG–DTG curve of [(nor)(PA)] charge-transfer complex.

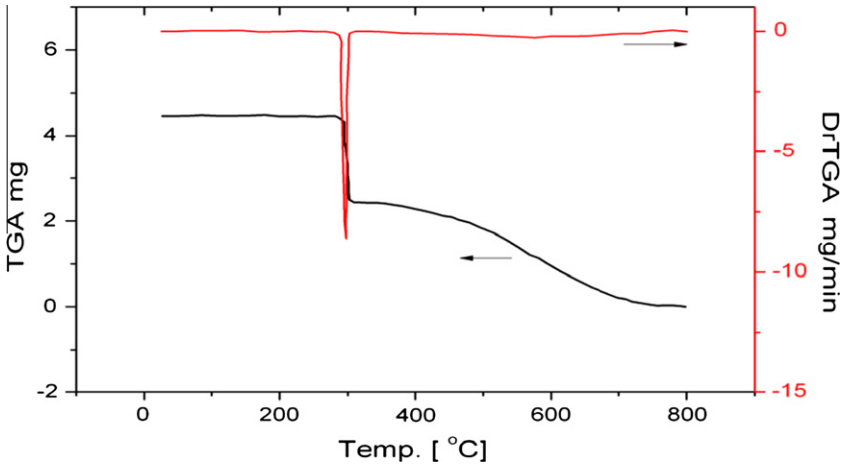


Fig. 5b. TG–DTG curve of [(cip)(PA)] charge-transfer complex.

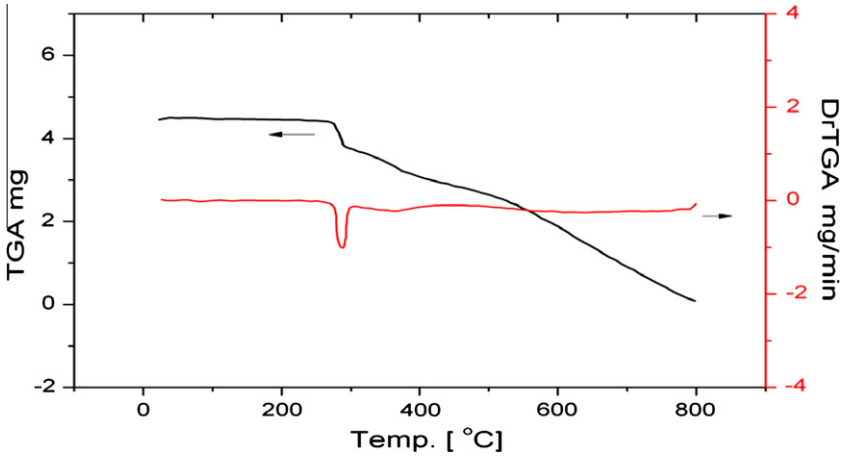


Fig. 5c. TG–DTG curve of [(nor)(DNB)] charge-transfer complex.

i. Horowitz and Metzger (HM) approximation method [29].

Consider the following relation [29]:

$$\ln[-\ln(1-\alpha)] = \frac{E}{RT_m}\Theta \ldots \quad (8)$$

where α, is the fraction of the sample decomposed at time t and $\Theta = T - T_m$.A plot of $\ln[-\ln(1-\alpha)]$ against Θ was found to be straight line the slope of which is E, and Z can be deduced according to the relation:

$$Z = \frac{E\varphi}{RT_m^2}\exp\left(\frac{E}{RT_m}\right)\ldots \quad (9)$$

where φ is the linear heating rate. The order of reaction, n, can be calculated regarding the following relation:

Table 6
Kinetic parameters of [(nor)(PA)], [(cip)(PA)] and [(nor)(DNB)] CT-complexes.

Method	n	Parameter					r
		E (kJ mol^{-1})	Z (s^{-1})	ΔS (J mol^{-1} K^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	
[(nor)(PA)]							
HM	1	470	4.82×10^{39}	−509	471	163	0.9669
CR	1	456	3.98×10^{23}	−501	423	154	0.9666
[(cip)(PA)]							
HM	1	123	1.72×10^{9}	−73.6	118	160	0.9992
CR	1	67.1	1.18×10^{4}	−172	134	146	0.9961
[(nor)(DNB)]							
HM	1	27.2	1.03	−250	22.6	160	0.9966
CR	1	23.2	1.42×10^{1}	−266	18.7	165	0.9973

n = number of decomposition steps.

$$n = 33.64758 - 182.295\alpha_m + 435.9073\alpha_m^2 - 551.157\alpha_m^3 + 357.3703\alpha_m^4 - 93.4828\alpha_m^5 \quad (10)$$

where α_m is the fraction of the substance decomposed at T_m.

ii. Coats and Redfern (CR) integral method [30].

For first-order reactions, the following equation of Coats–Redfern is fulfilled:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{ZR}{\varphi E}\right) - \frac{E}{RT}\cdots \quad (11)$$

A plot of $\ln[\frac{-\ln(1-\alpha)}{T^2}]$ against $1/T$ was found to be linear. From the slope E was calculated and Z can be deduced from the intercept. The enthalpy of activation, ΔH, and the free enthalpy of activation, ΔG, can be calculated via the equations:

$$\Delta H = E - RT_m; \quad \Delta G = \Delta H - T_m\Delta S \ \ldots \quad (12)$$

The evaluated kinetic parameters, using of the above two mentioned methods by graphical means, are listed in Table 6. The satisfactory value of correlation coefficient ($r \sim 1$) in all cases indicates reasonable agreement between experimental data and the values of kinetic parameters.

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