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Spectroscopic and physical measurements on charge transfer complex of norfloxacin drug with iodine acceptor

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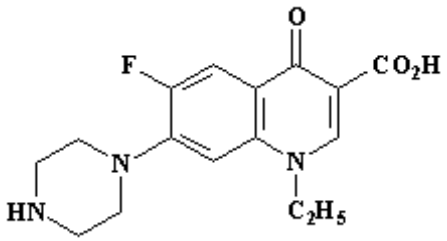
The charge-transfer complex of the norfloxacin (nor) donor with iodine (I_2) acceptor has been studied spectrophotometrically in chloroform at room temperature using absorption spectrophotometer. The results pointed to the formation of CT complex. The stoichiometry of the complex was determined. The ratio method between donor and acceptor was found to be 1:1 by molar ratio method. The 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, HNMR, mass spectra, UV-Vis techniques, elemental analyses (CHN) and TG-DTG/ DTA investigations were used to characterize the structure of charge-transfer complex. It was found that the CT interaction is associated with a proton migration from the donor to iodine followed by intermolecular hydrogen bond. In addition X-ray investigation was carried out to scrutinize the crystal structure of the complex.

Keywords: Norfloxacin, charge-transfer complexes, TG/DTG, IR, iodine.

1. INTRODUCTION

Norfloxacin (Formula I) is a synthetic chemo-therapeutic agent [1, 2] occasionally used to treat common as well as complicated urinary tract infections [3]. It is sold under various brand names with the most common being Noroxin. Norfloxacin is a second-generation synthetic fluoroquinolone (quinolone) developed by Kyorin Seiyaku .K.K. (Kyorin) [4].



Formula I: Norfloxacin (nor)

Charge-transfer complexes are known to take part in many chemical reactions like addition, substitution and condensation [5, 6]. These complexes have drawn great attention for the production of non-linear optical materials and electrical conductors [7-10]. Electron donor-acceptor (EDA) interaction is also important in the field of drug-receptor binding mechanism [11], in solar energy storage [12] and in surface chemistry [13], as well as in many biological fields [14]. On the other hand, the EDA reactions of certain π- acceptors have successfully been applied in pharmaceutical analysis [15]. For such wide applications extensive studies on CT-complexes of π- acceptors have been performed [16]. Charge-transfer complexes of organic species are intensively studied because of their special type of interaction, accompanied by transfer of an electron from the donor to the acceptor [17, 18]. Also, protonation of the donor from acidic acceptors is generally root for the formation of ion pair adducts [19-21]. The solid charge-transfer complexes formed between iodine and several types of electron donors such as aromatic hydrocarbons, polycyclic amine, mixed oxygen/nitrogen cyclic bases, aromatic/aliphatic amines have been studied and categorized [22-30]. Some of charge-transfer complexes have very interesting applications in the analysis of some drugs in pure form or in pharmaceutical preparations [31, 32].

The charge-transfer reaction of (nor) with I_2 has not yet been reported in the literature; therefore the aim of the present study was directed to investigate these reactions. The results of the elemental analysis for the norfloxacin charge-transfer complex are listed in Table 1. From the table, it can be seen that values found are in agreement with the calculated

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Table 1: Elemental analysis CHN and physical parameters data of the $[(nor)_2I^+].I_3^-$ CT-complex

Complexes	Mwt	C%		H%		N%		Physical data	
		Found	Calc.	Found	Calc.	Found	Calc.	Λm (μs)	mp (°C)
$[(nor)_2I^+].I_3^-$	1150	33.29	33.40	3.10	3.13	7.22	7.30	75	280

ones, and the composition of the CT-complex matches with the molar ratios obtained by photometric titration of (nor) and iodine σ-acceptors. This complex is insoluble in cold and hot water, but easily soluble in DMF and DMSO.

2. EXPERIMENTAL

Norfloxacin (MF= $C_{16}H_{18}FN_3O_3$), was of analytical reagent grade (Merck). The iodine acceptor was supplied from Aldrich. Stock solutions of norfloxacin or of iodine acceptor were freshly prepared and spectroscopic grade that used as received.

3.1. Synthesis of norfloxacin/iodine complex

The solid CT complex of (nor) with iodine was prepared by mixing (0.319 g, 1.0 mmol) of the donor in chloroform (10 ml), adding a solution of iodine (0.254 g, 1.0 mmol) in the same solvent (10 ml) and continuously stirring for about 4 h at room temperature. An orange yellow solid was isolated and the solution was allowed to evaporate slowly at room temperature. A solid complex was formed, washed several times with small amounts of chloroform, and dried under vacuum over anhydrous calcium chloride. The empirical formula of the complex $[(Nor)_2I]^+.I_3^-$ is $C_{32}H_{36}F_2N_6O_6I_4$ with molecular weight 1150 g/mol.

3.2.Instrumentation and physical measurements

3.2.1. Crystal structure.

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

3.2.2. Electronic spectra

The electronic spectra of the donors, acceptors and the resulting CT complexes were recorded in the region of 200-800 nm on a Jenway 6405 spectrophotometer with quartz cells, 1.0 cm path in length.

3.2.3. Infrared spectra

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

3.2.4. ^{1}H-NMR spectra

^{1}H-NMR spectra were obtained on a Varian Gemini 200 MHz spectrometer. ^{1}H-NMR data are expressed in parts per million (ppm), referenced internally to the residual proton impurity in DMSO solvent and the reported chemical shift, (m = multiplet, s = singlet and br = broad).

3.2.5. Mass spectra

The compositions of the complexes were confirmed from mass spectra at 70 eV taken on an AEI MS 30 mass spectrometer.

3.2.5. Thermal analysis

The thermal analysis (TGA/DTG/DTA) was carried in nitrogen atmosphere with a heating rate of 10ºC/min using a Shimadzu TGA-50H thermal analyzer.

4. RESULTS AND DISCUSSION

4.1. X-ray examination

For investigating the crystal structure of the obtained complex powdered samples were X-ray examined. In Fig. 1 the diffraction pattern is displayed, which reveals that the samples were in polycrystalline form. For the lack of structural data about the investigated materials, the CMPR program was applied in order to index the diffraction pattern [33]. Best fit of the diffraction pattern was carried out to estimate the unit cell and lattice parameters of norfloxacin: monoclinic unit cell with volume and lattice parameters 415.75 A^2, a=11.6535 A, b= 4.6922 A, and c= 7.6034 A for α= 90º, β= 124.046º and γ= 90º. Space group and average grain size were found to be P 2_1/m 1 1 and 109 nm, respectively.

4.2. *Electronic absorption spectrum of SZ/iodine system*

The UV-Vis absorption spectrum of the iodine complex was measured in $CHCl_3$ solvent. The complex was formed by adding X ml of 5.0×10^{-4} M iodine (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 norfloxacin. The volume of the mixtures in each case was completed to 10 ml with the $CHCl_3$ solvent. In the reaction mixture the concentration of (nor) was

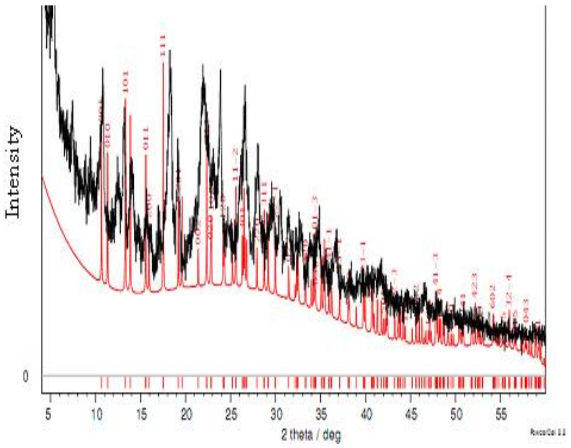


Fig. 1. X-ray diffraction pattern of norfloxacin with indexing.

kept fixed at 0.50×10^{-4} M, while the concentration of iodine was varied over the range from 0.125×10^{-4} M to 1.500×10^{-4} M. These concentrations produced (nor): I_2 ratios extending along the range from 1:0.25 to 1:3.00. Electronic absorption spectra of the 1:1 ratio in $CHCl_3$ together with the reactants I_2 and (nor) are shown in Figure 2.

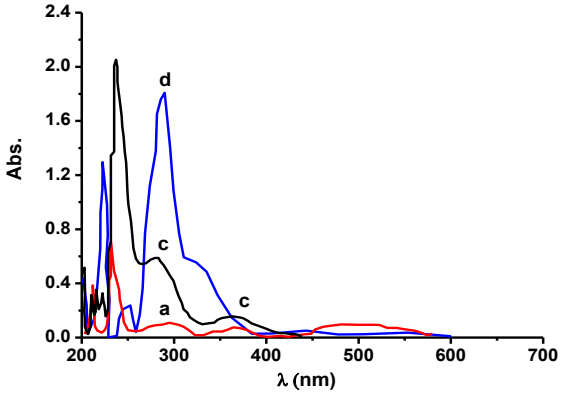


Fig. 2. Spectrum of electronic absorption of; norfloxacin-iodine reaction in $CHCl_3$, where (a) = acceptor (1.0×10^{-4}M), (c) = CT-complex and (d) = donor (1.0×10^{-4}M).

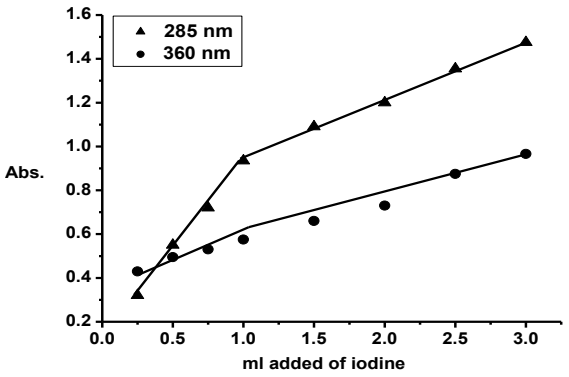


Fig. 3. Photometric titration curve for the norfloxacin-iodine system in $CHCl_3$ at 285 and 360 nm.

Characteristic absorption bands, which are not present in the spectra of the reactants free iodine and (nor), are shown in the spectra. These bands at about 360 and 290 nm were assigned to the CT-complex formed in the reaction. In other words, both (nor) and I_2 in the chloroform are not responsible for these bands. Table 2 gives the values of the absorbances obtained from photometric titrations based on the absorption bands at about 360 and 290 nm. Photometric titration curves based on these characteristic absorption bands are given in Figure 3. The photometric titration curve was obtained, according to the known methods, by plotting the absorbance against the ml added iodine σ-acceptor [33]. The equivalent points of this curve clearly indicate that the formed CT-complex between (nor) and iodine is 1:1. The formation of 1:1 complex was strongly supported by elemental analysis, mid-infrared, ^{1}H-NMR, mass spectra as well as by thermal analysis TG-DTG. However, the appearance of the two absorption bands around ≈ 360 and ≈ 290 nm is well known to be characteristic for the formation of the tri-iodide ion (I_3^-)[34-36]. Accordingly, the formed complex was formulated as $[nor_2I^+].I_3^-$.

Table 2. The electronic absorptions spectral data for nor-iodine CT-complex in $CHCl_3$ solvent (*1ml nor (5×10^{-4} M) + X ml iodine (5×10^{-4} M) + Y ml solvent = 10 ml*)

X ml of iodine	(nor : Iodine) ratio	Absorbance	
		285 nm	360 nm
0.25	1 : 0.25	0.32	0.43
0.50	1 : 0.50	0.55	0.49
0.75	1 : 0.75	0.72	0.53
1.00	1 : 1.00	0.94	0.57
1.50	1 : 1.50	1.09	0.66
2.00	1 : 2.00	1.20	0.73
2.50	1 : 2.50	1.36	0.88
3.00	1 : 3.00	1.48	0.97

It was of interest to study the effect of the solvent on the spectral intensities of the formed $[nor_2I^+].I_3^-$ complex. Calculations based upon the modified Benesi-Hildebrand equation, were executed for different (nor)-iodine ratios as follows [37]:

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

where C_a^o and C_d^o are the initial concentrations of the acceptor (I_2) and the norfloxacin donor, respectively. A is the absorbance of the definite bands at about 360 and 290 nm. Data for C_d^o of nor and C_a^o of (I_2), ($C_a^o + C_d^o$) and ($C_a^o . C_d^o$/A) in

Table 3. The values C_d^o, C_a^o, $C_d^o+C_a^o$ and $C_d^o.C_a^o/A$, for the nor-iodine system in $CHCl_3$ solvent

nor: Iodine ratio	C_d^o $\times10^{-4}$	C_a^o $\times10^{-4}$	$(C_d^o+C_a^o)$ $\times10^{-6}$	$(C_d^o.C_a^o)$ $\times10^{-8}$	$(C_d^o.C_a^o/A)$ $\times10^{-10}$	
					285 nm	360 nm
1 : 0.25	0.5	0.125	62.50	0.0625	0.19	0.14
1 : 0.50	0.5	0.250	75.00	0.1250	0.23	0.25
1 : 0.75	0.5	0.375	87.50	0.1875	0.26	0.35
1 : 1.00	0.5	0.500	100.0	0.2500	0.27	0.43
1 : 1.50	0.5	0.750	125.0	0.3750	0.34	0.57
1 : 2.00	0.5	1.000	150.0	0.5000	0.42	0.68
1 : 2.50	0.5	1.250	175.0	0.6250	0.46	0.71
1 : 3.00	0.5	1.500	200.0	0.7500	0.51	0.78

Table 4. Spectrophotometric results of the $[(nor)_2I^+].I_3$ complex in $CHCl_3$ solvent at 25°C

λ_{max} (nm)	E_{CT} (eV)	K ($l.mol^{-1}$)	ε_{max} ($l.mol^{-1}.cm^{-1}$)	f *10^3	μ*10^3	I_p	D	R_N	ΔG^o(25°C) $KJmol^{-1}$
360	3.45	7.0*10^4	220*10^4	0.02	0.40	10.00	4.70	0.980	27800

$CHCl_3$ solvent, are presented in Table 3. By plotting the $C_a^o.C_d^o/A$ values for each solvent against the corresponding $(C_a^o+C_d^o)$values, straight lines were obtained with a slope of 1/ε and intercept of 1/kε as shown in Figure 4 for the reaction in $CHCl_3$. The oscillator strength f was obtained from the approximate formula [38]:

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

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 4. From the data in Table 4 several conclusions may be drawn:

i) The $[(nor)_2I^+].I_3^-$ complex displays high values of both the equilibrium constant (K) and the extinction coefficient (ε). Such high value of (K) reflects the high stability of the (nor)/iodine complex as a result of the expected high donation ability of norfloxacin. On the other hand, the high value of (ε) of the (nor)/iodine CT-complex agrees quite well with the existence of a tri-iodide ion, I_3^-, which is known to have a high absorptivity value [34-36].

ii) The values of the oscillator strength, f, increase with increasing the dielectric constant (D) of the solvent. The general mechanism for the formation of $[(nor)_2I^+].I_3^-$complex was proposed as follows:

$$2nor+I_2 \rightarrow [nor]_2I^+.I^-$$

$$[nor]_2I^+.\ I^- + I_2 \rightarrow [(nor)_2I^+].I_3^-$$

The formation of the $[nor]_2I^+.I^-$ reaction intermediate is analogous to the well known species $[(donor)I]^+.I^-$ formed in the reaction of iodine with many donors [39-40].

The transition dipole moment (μ) of the norfloxacin CT-complex, Table 4, was calculated from the following equation [41]:

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

The ionization potential (I_p) of the free (nor) donor was determined according to the CT band of the iodine complex using the following relationship [42-43]:

$$I_p\ (ev) = 5.76 + 1.53\times10^{-4}\ \ \nu_{CT} \qquad (4)$$

The charge-transfer energy E_{CT} of the $[(nor)_2I^+].I_3^-$ complex was calculated using the following eq. [41]:

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

The molar extinction coefficient of the complex at the maximum of the CT absorption (ε_{max}) can be calculated according to Briegleb and Czekalla [44] as follows:

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

where λ_{CT} is the wavelength of the complexation band, R_N is the resonance energy (R_N), ν_{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 $[(nor)_2I^+].I_3^-$complex under study are shown in Table 4. The standard free energy change of complexation (ΔG^o) was calculated from the association constants by the following equation [45]:

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

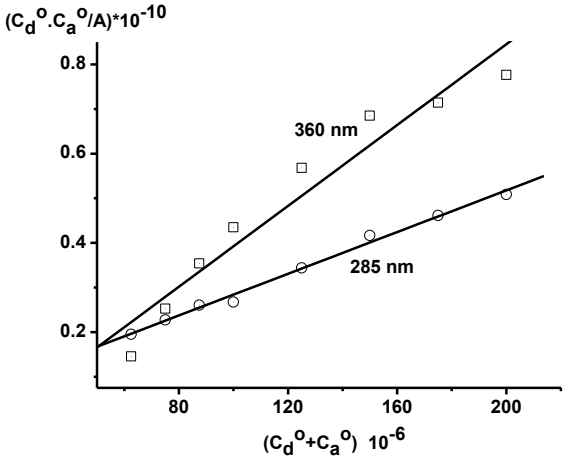


Fig. 4. The plot of (C_d^o+C_a^o) values against (C_d^o.C_a^o/A) values for the norfloxacin-iodine system in $CHCl_3$ at 360 and 285 nm.

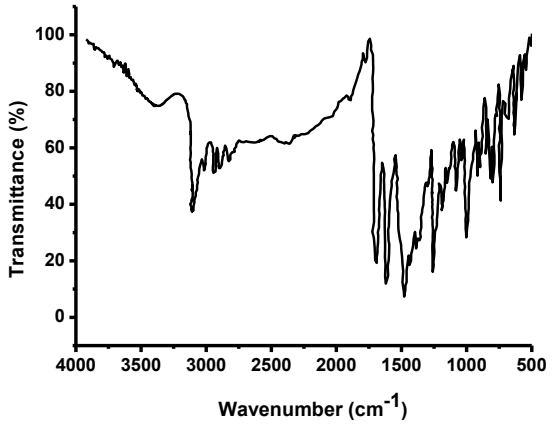


Fig. 5: Infrared spectra of $[(nor)_2I^+].I_3^-$ charge-transfer complex.

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 different solvents at room temperature. The values thus calculated are presented in Table 4.

4.3. *Infrared spectra of the $[(nor)_2I^+].I_3^-$*

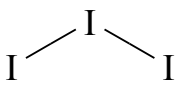
The mid-infrared spectra of norfloxacin and the formed CT-complex, $[(nor)_2I^+].I_3^-$, were recorded from KBr discs. These spectra are shown in Figure 5. The spectral bands, assigned to their vibrational modes, are given in Table 5. As expected, the bands characteristic for the norfloxacin unit in the $[(nor)_2I^+].I_3^-$ CT-complex are displayed with small changes in band intensities and frequency values. For example, the ν(N-H) vibrations of -NH occur at 3400-3200 cm^{-1} for free (nor) due to ν_{as}(NH) and ν_s(NH), respectively. The hypsochromic effect (decreasing in the intensity) of ν(NH) vibrations in case of the iodine complex rather than in norfloxacin alone, as well as the presence of a new band at 3134 cm^{-1} with strong intensity point to the formation of a hydrogen bond. Such changes clearly indicate that the –NH group of the norfloxacin donor participates in the complexation process with iodine. On the other hand, the existence of a few bands at around 2700-2400 cm^{-1} (hydrogen bonding) in the $[(nor)_2I^+].I_3^-$ complex [46], strongly confirms the mode of interaction between (nor) and iodine through the hydrogen atom of –NH as (N-H---I).

The geometry of I_3^- in $[(SZ)_2]I^+.I_3^-$ may belong to one of the two structures: linear structure with ($D_{\infty h}$) symmetry and non-linear structure with (C_{2v}) symmetry. The linear I_3^- ion is shown in formula (II). It possesses an infinite rotation axis C_∞, an infinite number of C_2 axes, an infinite inversion axis S_∞, an infinite number of vertical planes $\infty\sigma_v$, a horizontal plane of symmetry σ_h, and a center of symmetry. The C_2 axes are perpendicular to C_∞, and thus it belongs to $D_{\infty h}$ symmetry.

I—I—I

(**II**)

The non-linear triiodide I_3^- ion formula (**III**) has two fold axis of symmetry, C_{2v}, and two σ_v planes of symmetry, thus it belongs to C_n, symmetry.



(**III**)

Accordingly, the number of vibrations (Γ_{vib}) for the non-linear I_3^- ion with C_{2v} symmetry is distributed as follows:

$$\Gamma_{vib} = 2A_1 \text{ (IR and R)} + B_2 \text{ (IR and R)}$$

where IR and R represent the infrared and Raman activities, respectively. Formula III describes the nature of these vibrational motions of the non-linear I_3^- ion with C_{2v} symmetry.

4.4. *^{1}H-NMR spectrum of $[(nor)_2I^+].I_3^-$ complex*

^{1}HNMR spectra of the (nor) free donor and the $[(nor)_2I^+].I_3^-$ CT-complex in DMSO at room temperature were measured. The chemical shifts

Table 5. Infrared frequencies[(a)] (cm^{-1}) and tentative assignments for norfoloxacin donor and $[(nor)_2I^+].I_3^-$ complex.

Nor	$[(nor)_2I^+].I_3^-$	Assignments
3399 ms	3421 w,br	ν(N-H) + ν(O-H)
3267 vw, 3228 vw 3189 vw,	3134 s, 3048 w	ν (C-H)
3130 vw 3021 w, 2927 m	2969 w, 2924w	ν (-$^+$N-H…I); hydrogen bond
	2856 w, 2662 w	
	2411 w, 2371 w	
1727 sh, 1716 ms	1705 vs	ν(C=O): (COOH)
1630 vs, 1552 w	1628 vs	ν(C=O) + $\delta_b(H_2O)$
		Phenyl breathing modes
1482 vs, 1454m 1396 s	1488 s, 1445 vw	CH; deformation of –CH_2–
	1396 w, 1373 w	
1307 vw	1308 w	$\delta_b(CH_2)$
1277 vw, 1263 s 1248 vw	1265 vs	ν(C-C)
1201 m	1197 m	ν(C-O)
1192 m		ν(C-N)
1153 vw, 1142 w 1132 w, 1115	1160 w, 1140 vw	$\delta_r(CH_2)$
w 1095 m, 1076 m	1086 ms, 1064 mw	
1051 vw, 1036 ms 1024 w, 1005	1008 s	
m		
982 m		
972 w, 935 ms	924 ms, 903 ms	CH- bend; phenyl
916 m, 899 m	857 ms, 823 ms	
887 m, 858 w	803 ms	
823 ms, 804 ms		
750 s, 706 m	750 s, 712 w	$\delta_b(COO^-)$
667 w, 631 w,br, 569 ms, 524 w	691 m, 643 ms	ring deformation
499 m, 474 m	590 ms, 558 w	
453 vw, 430 ms	521 vw, 496 ms	
	442 ms, 409 m	

(a): s = strong, w = weak, m = medium, sh = shoulder, v = very, br = broad; (b): ν, stretching; δ, bending.

(ppm) of proton NMR for the detected peaks were assigned and listed in Table 6. Evidently, the results obtained from elemental analysis, infrared spectra, and photometric titrations agreed with the ^{1}HNMR spectra to interpret the mode of interaction between donor and acceptor as follows:

i) In the $[(nor)_2I^+].I_3^-$ CT complex, the signal assigned to the H proton of -NH of norfloxacin at ~2.00 ppm was shifted upfield due to migration from donor to acceptor as –NH…I (formula IV).

ii) The shift of most signals in the $[(nor)_2I^+].I_3^-$ CT complex is due to the interaction between donor and acceptor. On the other hand, there is duplication in all bands due to the presence of two norfloxacin moieties.

4.5. Mass spectrum of $[(nor)_2I^+].I_3^-$ complex

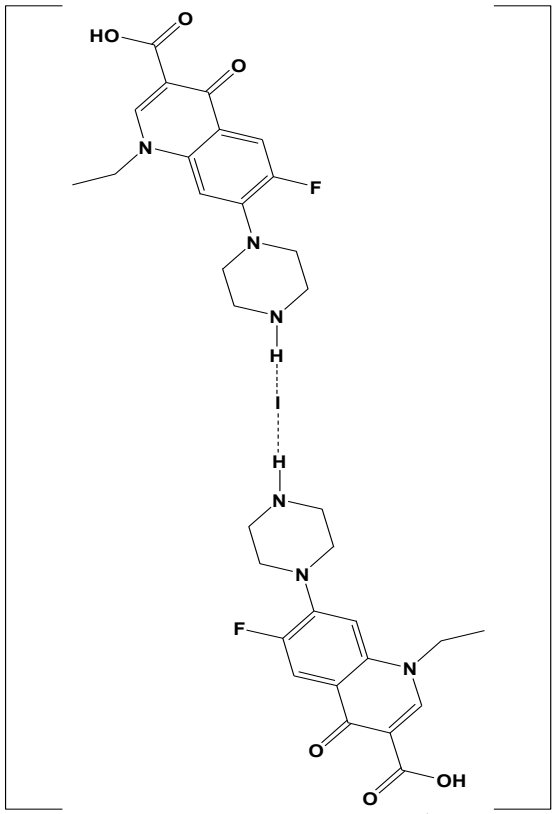
Mass spectrometry was applied in order to study the main fragmentation routes of the $[(nor)_2I^+].I_3^-$ charge-transfer complex. Differences in fragmentation were caused by the nature of the attached acceptor through the intermolecular hydrogen bond between norfloxacin and iodine, while the observed peaks assigned to iodine and norfloxacin at *m/z* 128 (M+1) and 319 amu, were detected in the fragmentation of $[(nor)_2I^+].I_3^-$ CT-complex. The basic peak observed at *m/z*= 275 for $[(nor)_2I^+].I_3^-$ CT-complex was assigned to the loss of a COOH group. The intensities of these peaks give an idea of the stabilities of the fragments.

4.6. *Thermal analysis studies*

Norfloxacin melts at 232^{o}C with simultaneous decomposition [47]. The first mass loss was observed at 125 ^{o}C in the TG profile. The TG/DTG profiles of the ligand are shown in Figure 6A. From the TG curve it appears that the sample decomposes

Table 6: ^{1}HNMR spectral data of free nor and $[(nor)_2I^+].I_3^-$ complex

Nor	[(nor)2I+].I3$^-$	Assignments
1.13	1.218	δ H, -CH3
2.0	1.387, 1.419,	δ H, -NH; Piperazine
	1.453	
2.78, 3.10,	3.349, 3.532,	δ H, -CH2; Piperazine
3.47	4.591	δ H, -CH2; -CH2CH3
	4.626	
5.93, 7.12,	7.254, 7.219,	δ H, -CH aromatic
8.01	7.878	
	7.944, 8.809	
11.00	8.948	δ H, -COOH



Formula IV: The structure of $[(nor)_2I^+].I_3^-$ CT complex

in three steps over the range 25-726 °C. The first decomposition step occurs between 25-270 °C with a mass loss of 8.38%; the second decomposition step starts at 270 °C and ends at 575 °C with a 69.80% mass loss. The next decomposition step occurs in the range 575-726 °C with a maximum at 650 °C and is accompanied by a weight loss of 19.56 %. Such a trend, which may be attributed to the loss of a pyrrole ring, ($2C_2H_2$+1/2N_2+1/2H_2), is in reasonable agreement with the theoretical value of 21.00 %.

In Figure 6B, the $[(nor)_2I^+].I_3^-$ CT-complex was thermally decomposed in four successive decomposition steps within the temperature range 25-800 °C. From Figure 6C (DTA curve), the decomposition steps located at 108, 217, 347 and 578 °C with experimental weight losses of 3.41, 19.66, 26.57 and 46.28%, respectively, were attributed to the liberation of two I_2 molecules and a $C_{25}H_{36}F_2N_6O_6$ organic moiety, with a contentious decomposition of the donor molecule to final residual carbons.

4.7. *Kinetic studies*

Three different methods were applied for the evaluation of the kinetic parameters as follows:

i) Freeman and Carroll (FC) differential method [48].

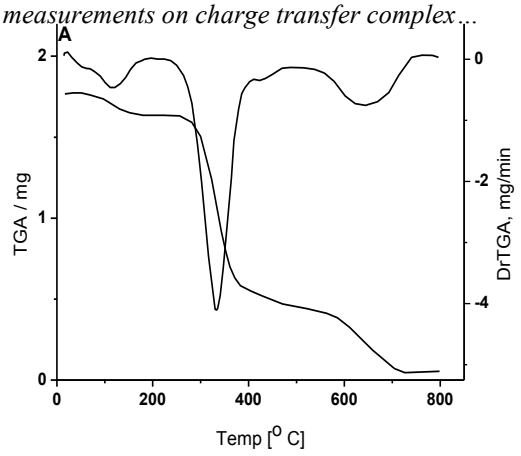


Fig. 6A. TG-DTG curve of norfloxacin free ligand.

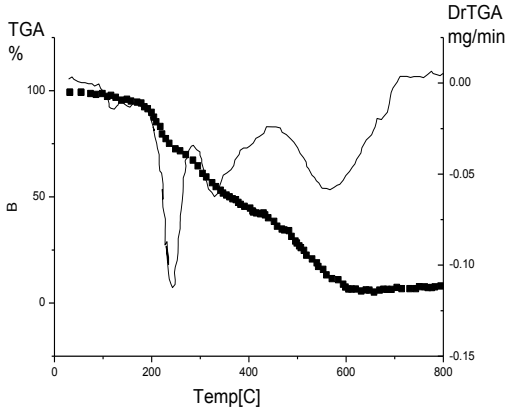


Fig. 6B. TG-DTG curve of $[(nor)_2I^+].I_3^-$ charge-transfer complex.

By combining the usual first-order equation with the Arrhenius equation, one gets:

$$\ln\left[\frac{dw/dt}{w_r}\right] = \ln Z - \frac{E}{RT}, \qquad (8)$$

where w is the total loss in weight up to time, t, $w_r = w_f - w$, w_f is the weight loss at the completion of the reaction, R is the gas constant and

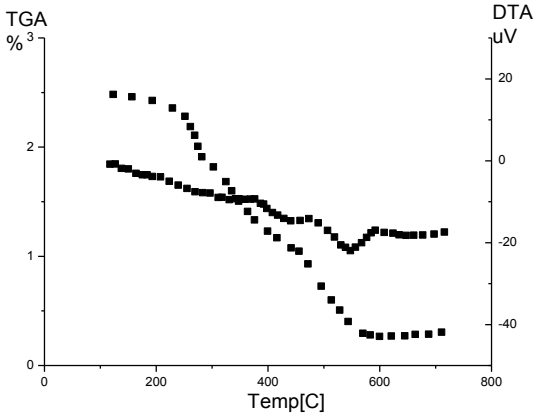


Fig. 6C. TG-DTA curve of $[(nor)_2I^+].I_3^-$ charge-transfer complex.

Table 7: Kinetic parameters of norfloxacin and $[(nor)_2I^+].I_3^-$CT-complex.
7a: nor

Method	n	Parameter					r
		E / kJmol^{-1}	Z / s^{-1}	ΔS / Jmol^{-1}K^{-1}	ΔH / kJmol^{-1}	ΔG / kJmol^{-1}	
HM	1	96.6	8.68*10^1	-37.9	93.3	108	0.9817
CR	1	93.6	2.00*10^1	-50.1	90.3	110	0.9853

7b: $[(nor)_2I^+].I_3^-$

Method	n	Parameter					r
		E / kJmol^{-1}	Z / s^{-1}	ΔS / Jmol^{-1}K^{-1}	ΔH / kJmol^{-1}	ΔG / kJmol^{-1}	
HM	1	137	7.93*10^4	-62.31	112	133	0.9932
CR	1	141	4.21*10^6	-70.33	130	141	0.9943

(dw/dt) is the weight-time gradient. A plot of $\ln\left[\frac{dw/dt}{w_r}\right]$ against $1/T$ was found to be linear. The energy of activation, E, was calculated from the slope while the pre-exponential factor, Z, was calculated from the intercept. The entropy of activation ΔS, was obtained from the following equation:

$$\Delta S = R\ln\left(\frac{Zh}{K_B T_m}\right) \qquad (9)$$

where K_B is the Boltzmann's constant, h is the Planck's constant and T_m is the DTG peak temperature.

ii) Horowitz and Metzger (HM) approximation method [49].

The following relation was derived [49]:

$$\ln\left[-\ln(1-\alpha)\right] = \frac{E}{RT_m}\Theta \qquad (10)$$

where α is the fraction of the sample decomposed at time t and $\Theta = T - T_m$.

A plot of $\ln\left[-\ln(1-\alpha)\right]$ against Θ was found to be straight line the slope of which is E, and Z can be deduced according to the relation:

$$Z = \frac{E\varphi}{RT_m^2}\exp\left(\frac{E}{RT_m}\right) \qquad (11)$$

where φ is the linear heating rate, the entropy of activation ΔS, was calculated using Equation (9). The order of reaction, n, can be calculated regarding the following relation [50]:

$$n = 33.64758 - 182.295\alpha_m + 435.9073\alpha_m^2 - 551.157\alpha_m^3 + 357.3703\alpha_m^4 - 93.4828\alpha_m^5 \quad \text{....(12)}$$

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

iii) Coats and Redfern (CR) integral method [51].

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

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{ZR}{\varphi E}\right) - \frac{E}{RT} \qquad (13)$$

A plot of $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ 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 from the equations

$$\Delta H = E - RT_m \; ; \; \Delta G = \Delta H - T_m \Delta S \quad . \qquad (14)$$

The kinetic parameters evaluated using two of the above mentioned methods are listed in Table 7. The satisfactory values of the correlation coefficients (~1) in all cases indicate a good agreement with the experimental data. The values of the kinetic parameters are reasonable and in good agreement.

5. CONCLUSIONS

The crystal structure of Norfloxacin was recognized to be monoclinic with lattice constants a=11.6535 A, b= 4.6922 A, and c= 7.6034 A for α= 90°, β= 124.046° and γ= 90°. Space group and average grain size were found to be P 2_1/m 1 1 and 109 nm, respectively. The upfield shift in the NMR spectrum was attributed to the migration from donor to acceptor. Duplication in the NMR spectrum was ascribed to the existence of two Norfloxacin moieties. The disappearance of a COOH group was confirmed by the presence of a peak at m/z=275 in the mass spectrum. Kinetic parameters, such as E, z, ΔS, ΔH and ΔG were estimated.

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СПЕКТРОСКОПСКИ И ФИЗИЧНИ ИЗМЕРВАНИЯ НА КОМПЛЕКС С ПРЕНОС НА ЗАРЯД НА МЕДИКАМЕНТА НОРФЛОКСАЦИН С ЙОДЕН АКЦЕПТОР

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(Резюме)

Комплексът с пренос на заряд на норфлоксацин (нор) като донор с йоден (I_2) акцептор е изследван спектрофотометрично в хлороформ при стайна температура с абсорбционен спектрофотометър. Резултатите показват формиране на комплекс с пренос на заряд. Определена е стехиометрията на комплекса. Отношението между донор и акцептор е определен като 1:1 чрез метода на моларното отношение. Направена е оценка на константата на образуване (K_{CT}), моларния коефициент на екстинкция (ε_{CT}), стандартната свободна енергия (ΔG^o), силата на осцилатора (f), диполния момент на прехода (μ), енергията на резонанса (R_N) и потенциала на йонизация (I_D). Използвани са техниките с IR, HNMR, мас-спектри, UV-Vis, елементен анализ (CHN) и TG-DTG/ DTA изследвания за охарактеризиране на структурата на комплекса с пренос на заряд. Установено е, че взаимодействието с пренос на заряд е свързано с миграция на протон от донора към йода последвана от междумолекулна водородна връзка. В допълнение е проведено изследване с Рентгенови лъчи за изучаване на кристалната структура на комплекса.