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Charge Transfer Reaction of Novel Crizotinib with N – Bromo succinimide: A Spectrophotometric and Spectroscopic study

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Abstract: Comprehending the charge transfer process between bioactive molecules and inorganic or organic molecules is noteworthy as this interaction can be utilized to decipher bioactive molecule - receptor interactions. A thorough spectrophotometric study has been performed to investigate the complexation science of the Crizotinib (CZT) with N - Bromo Succinimide (NBS) as π - acceptor. The molecular structure, spectroscopic characteristics, and the interactive modes have been derived from UV–Vis, FT-IR spectra. The binding ratio of complexation has been determined to be 1:1 for NBS with CZT. Benesi–Hildebrand method was applied to estimate the spectroscopic and physical data. The association constant (K), extinction coefficient (ε_{max}), ionization potential (IP), the energy of the charge transfer complex ($h\nu_{CT}$), resonance energy (R_N), dissociation energy (W), and standard Gibbs energy (ΔG^0) have been computed.

INTRODUCTION:

Lung cancer has long been known as the most widely recognized helpless ailment stayed as the reason for disease-related deaths around the world, including 1.61 million new cases and 1.38 deaths in 2008 alone, registering 12.7% of additional cancers and 18.2% of cancer mortality[1]. Around 85% of lung cancer growths are non-small cell lung cancer (NSCLC) and most patients are diagnosed at a propelled stage.[2]; The 5-year survival for patients in the USA with NSCLC is around 16%. Current medicines for NSCLC may broaden endurance however are once in a while remedial [3].

Crizotinib (CZT) 3-[(1R)-1-(2,6-dichloro-3-fluorophenyl) ethoxy]-5-(1-piperidin-4-ylpyrazol-4-yl) pyridin-2-amine is a novel anti lung cancer drug acting as an ALK (Anaplastic Lymphoma Kinase) & ROS 1 (C- ROS, Oncogene 1) inhibitor; it has been endorsed by FDA on August 26, 2011, under the trade name of xalkori capsules, made by Pfizer, Inc. for the treatment of patients with locally advanced or metastatic Non-Small Cell Lung Cancer (NSCLC) i.e., ALK-positive as detected by an FDA endorsed test. Further clinical trials on CZT are under process to test its safety and efficacy in Anaplastic Large Cell Lymphoma, Neuroblastoma and other propelled strong tumors in both grown-ups and Children.

CZT is presently used to exert its effects through modulation of the growth; relocation and intrusion of malignant cells. Besides, different investigations recommend that CZT might also act via inhibition of Angiogenesis, in malignant tumours, which is of great interest in order to show how this novel CZT is noteworthy.

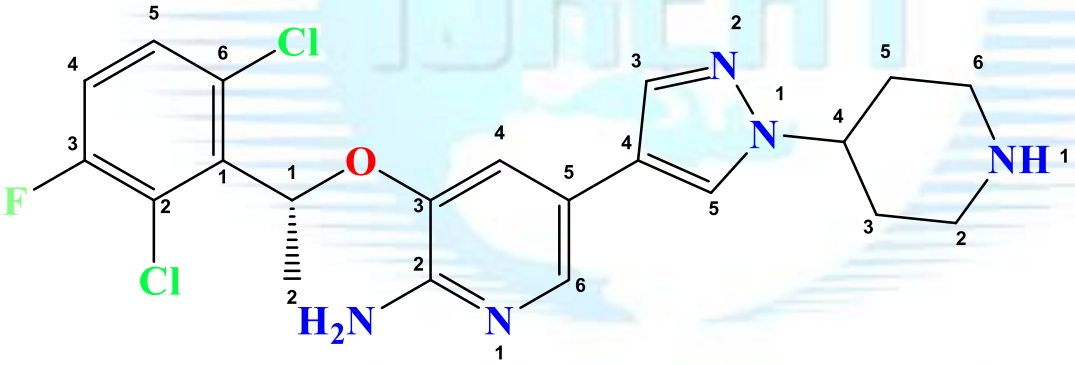
Available literature on this subject reveal that the electron donating properties of CZT and its Charge Transfer (CT) reactions have not been much investigated so far.

These findings about CZT prompted us to investigate the CT reaction of CZT with N-Bromo succinimide,NBS(π-
acceptor)

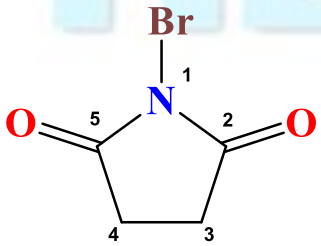
The CT complexes are identified to take part in many chemical reactions like addition, substitution, condensation, etc, Electron donor-acceptor CT interaction is also important in the field of drug receptor binding mechanism[4], as well as in many biological fields. Taking into account, this, CT reactions of certain π-acceptors have been effectively used in pharmaceutical analysis. The CT complexes (CTCs) of organic species are arduously studied on account of their special type of interaction which is accompanied by a transfer of an electron from donor to acceptor. Additionally, protonation of a proton from acidic receptors is generally routed for the formation of the ion pair adducts. The π-acceptors have various applications as analytical reagents. They have been used for the spectrophotometric determination of many drugs in pharmaceutical formulations.

Inasmuch all these aspects, it is proposed to investigate the charge transfer complex (CTC) of CZT with NBS.

Structures of CZT and NBS



CRIZOTINIB (CZT)



N-BROMOSUCCINIMIDE (NBS)

1 Experimental Methodologies

1.1 Chemicals

All the chemicals were used of analytical grade. NBS (Finar, India, immaculateness > 98%) and Dimethyl sulfoxide, DMSO (Finar, India, immaculateness> 99.9%) were utilized without any further purification. The CZT was procured from Meruvax pharmaceuticals, Hyderabad. The immaculateness of CZT as specified by the producers was >99%, which was confirmed by its melting temperature. The CZT was used with no further purging.

1.2 Synthesis of CZT–NBS CT complex

The CZT and NBS of 1 mmol each (1:1) were precisely weighed on Dhona 160 D analytical balance and transferred them into porcelain mortar and truncated the blend carefully in the presence of a few drops of methylene chloride solvent. Then dried the obtained reaction mixture by continuous suction and transferred them into a dry beaker. The beaker was stored overnight in a desiccator filled with activated anhydrous calcium chloride, then transferred the dried solid brown coloured powder containing CZT–I_2 CTC into a clean vial. The vial was topped well to shield from soggy air.

2 Instruments

The electronic absorption spectra of the CZT, NBS, and resulting CTC were recorded over a wavelength range of 200–800 nm using a UV-2600 Shimadzu UV-VIS Spectrophotometer. The instrument was equipped with a quartz cell with a 1.0 cm path length. The FT-IR spectra within the range of 4000–250 cm–1 for the solid powder of free CZT and its CT Complex with NBS were recorded on a Shimadzu FT-IR Prestige-21 spectrophotometer with 40 scans at 4 cm–1 resolution.

3 Spectrophotometric Study

3.1 Preparation of Experimental Solutions

Stock solutions of CZT (donor) and NBS (acceptor) at a concentration of 5 x 10^{-3} mol·L^{-1} were freshly prepared before each series of measurement by dissolving accurately weighed amounts in an appropriate volume of DMSO. The stock solutions of donor and acceptor were protected from light. The solutions for spectrophotometric measurements were freshly prepared by mixing appropriate volumes of donor and acceptor stock solutions immediately before recording the spectra.

3.2 Experimental Measurements

To determine the stoichiometry of the CZT (donor) and NBS (acceptor) interactions, various molar ratios were examined by applying Job's method of continuous variations[5-6] and photometric titration measurements. These titrations monitored the detectable CT bands during the reactions of NBS with donor. Briefly, 0.25, 0.50, 0.75, 1.00, 1.50, 2.0, 2.50, 3.00, 3.50 or 4.00 mL of a standard solution (5 x 10^{-4} mol·L^{-1}) of the appropriate donor in DMSO solvent was added to 1.00 ml of the acceptor at 5 x 10^{-4} mol·L^{-1}, dissolved in the same solvent. The final volume of the mixture was made to 5 ml. The concentration of the acceptor (C^0_a) was maintained constant at 5.0 x 10^{-4} mol·L^{-1}, while the concentration of the donor (C^0_d) varied from 0.25 x 10^{-4} mol·L^{-1} to 4.0 x 10^{-4} mol·L^{-1} to produce solutions with a (donor: acceptor) molar ratio that varied from 1:4 to 4:1, for the 1:2 complex. The absorbance of complex was plotted against the volume of the added acceptor.

3.3 Calculations – Background

The physical spectroscopic data of the resulted CT complexes were computed, the association constant (K) and the molar extinction coefficient (ε_{max}) were determined spectrophotometrically using the Modified 1:2 Benesi–Hildebrand equation[7] for the 1:2 CT complex with NBS.

Table 1 Benesi–Hildebrand data of the CZT-NBS CT complex

C^0_a x 10^{-4}	C^0_d x 10^{-4}	Absorbance	$(C^0_a)^2 C^0_d$ / A x 10^{-12}	C^0_a ($4C^0_d + C^0_a$) x 10^{-8}
0.25	5	0.657	2.097	5.062
0.5	5	0.750	7.530	10.250
0.75	5	0.835	15.368	15.562
1.0	5	0.926	25.000	21.000
1.5	5	0.938	48.900	32.250
2.0	5	0.956	76.920	44.000
2.5	5	0.968	97.170	56.250
3.0	5	0.976	150.000	69.000
3.5	5	0.985	189.620	82.250
4.0	5	0.998	231.880	96.000

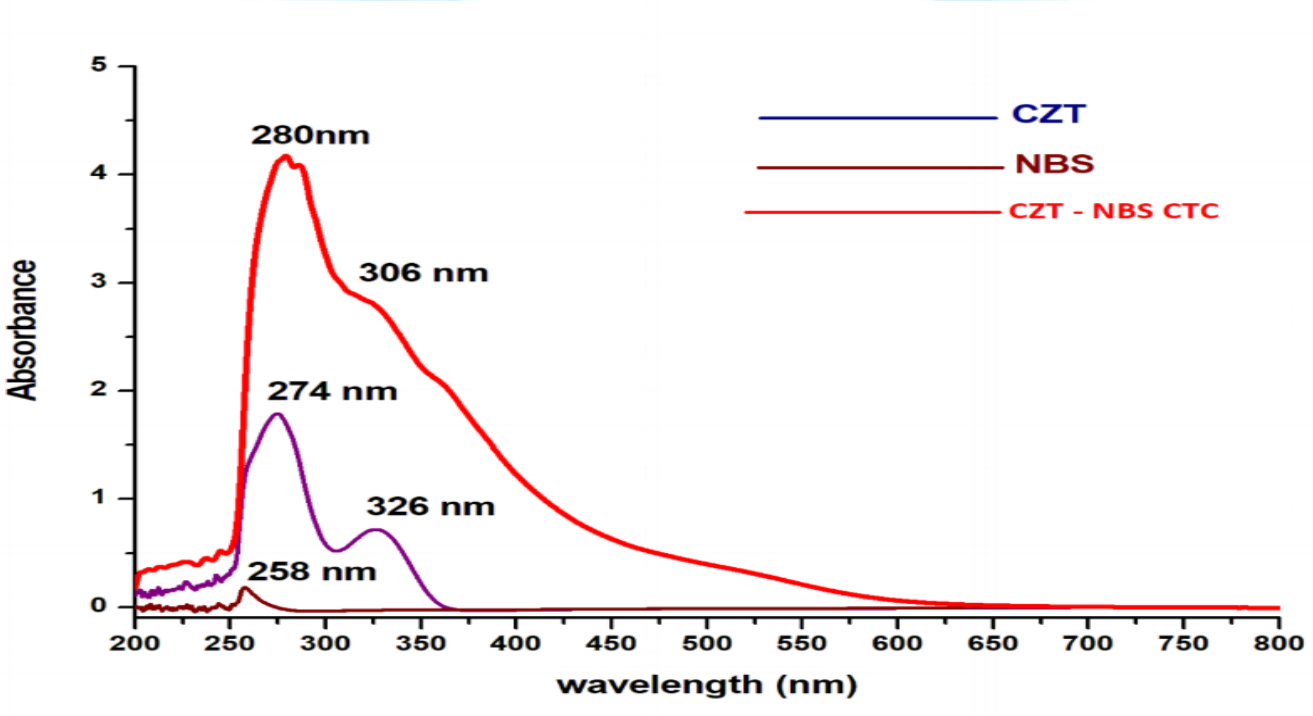
Modified Benesi–Hildebrand (1:2) equation

$$(C^0_a)^2 C^0_d/A = 1/K\varepsilon + 1/ \varepsilon C^0_a (4C^0_d + C^0_a) \text{ ---------- (2)}$$

Where, C^0_a and C^0_d are the initial concentrations of the acceptor and donor, respectively, and A is the absorbance of the CT band. By plotting the $(C^0_a)^2 C^0_d/A$ for the 1:2 CT complex as a function of the corresponding values C^0_a $(4C^0_d + C^0_a)$, a straight line is obtained with a slope of 1/ ε and an intercept at 1/K ε.

4. Results and discussion

4.1 Electronic Spectra



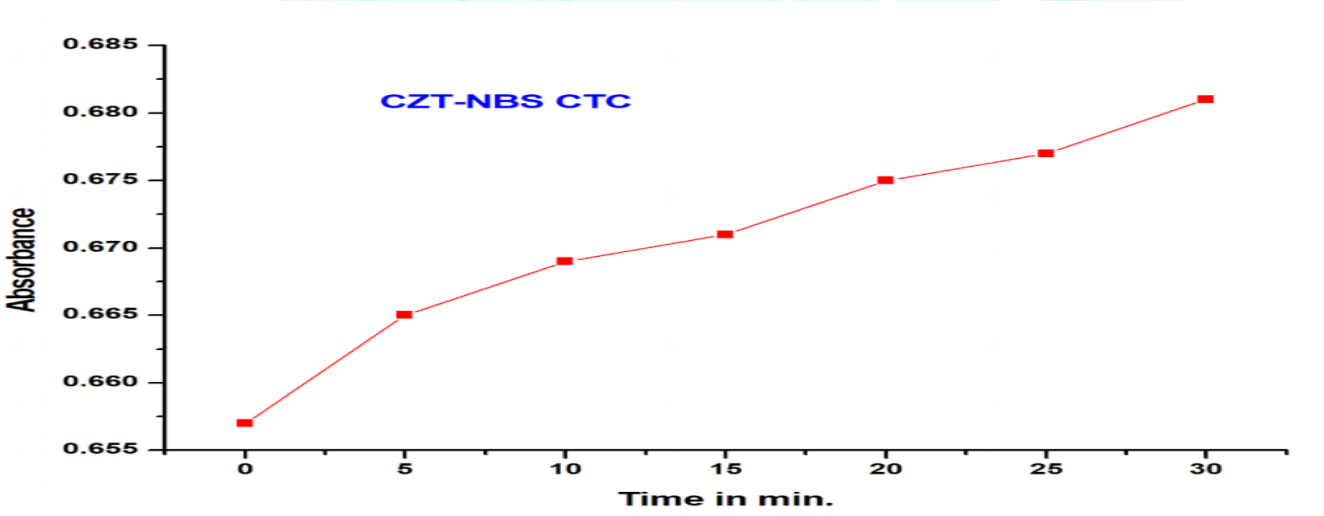
it has highest absorption intensity (Figure 1). Polar solvent such as DMSO has been chosen as the solvent to promote the complete transfer of electron from CZT (donor) to the NBS (acceptor).

4.2 Conductance measurements of freshly prepared experimental solutions

Conductimetry has often been employed to study the interactions of CT complexes [8,9]**.** In the present study, the conductivity measurements of CZT (donor) and its synthesized CT complexes with NBS were performed in DMSO solvent at $5x10^{-3}$ M using Systronics 304 conductivity meter. The conductance values of free donor was found to be 7 Ω^{-1} cm^2 $mole^{-1}$ and for free acceptor NBS was found to be 20 Ω^{-1} cm^2 $mole^{-1}$ while, the conductance values of CZT-NBS complex was found to be 92 Ω^{-1} cm^2 $mole^{-1}$ respectively, this result suggest that the resulted complex have electrolytic behaviour. This data reveals the formation of dative D^+- A^- complex between CZT (donor) and NBS (acceptor) under the acid-base theory. The increase in conductivity was observed with elapse of time, may be due to the fact that the CT complex formed between donor and acceptor might have undergone dissociation into ionic intermediate in solvents of sufficient high dielectric constant give rise to appreciable conductivity.

4.3. Effect of reaction time

The optimum reaction time was determined by observing the light-yellow colour development at ambient temperature (25±1°C). The complete colour development was attained instantaneously with compound investigated, and the colour remained stable for 24 hrs. And it is observed that as the time increases absorbance values increase (**Fig. 2**), which suggest the stability of the CZT-NBS complex.



4.4. Stoichiometry of the interaction

The stoichiometry of the formed CZT-NBS complex was determined by applying Job's method of continuous variations (**Fig.3**), the symmetrical curves with a maximum at 0.4 mole fraction indicated the formation of 1:2 complex (**Fig.4**). The spectrophotometric titration measurements were also performed for the determination of stoichiometry of the formed CT complex. The electronic spectra of the CZT-NBS complex was recorded with varying concentrations of acceptor, while, concentration of donor is kept constant. The stoichiometry of the complex was determined graphically by plotting the absorbance as a function of the volume of donor (in mL), where two straight lines are produced intercepting at 1:2 ratio for complex. Representative spectrophotometric titration plot based on the characterized absorption bands are shown in **Fig. 3.** The results show the good interaction between NBS acceptor and CZT donor considered in the study.

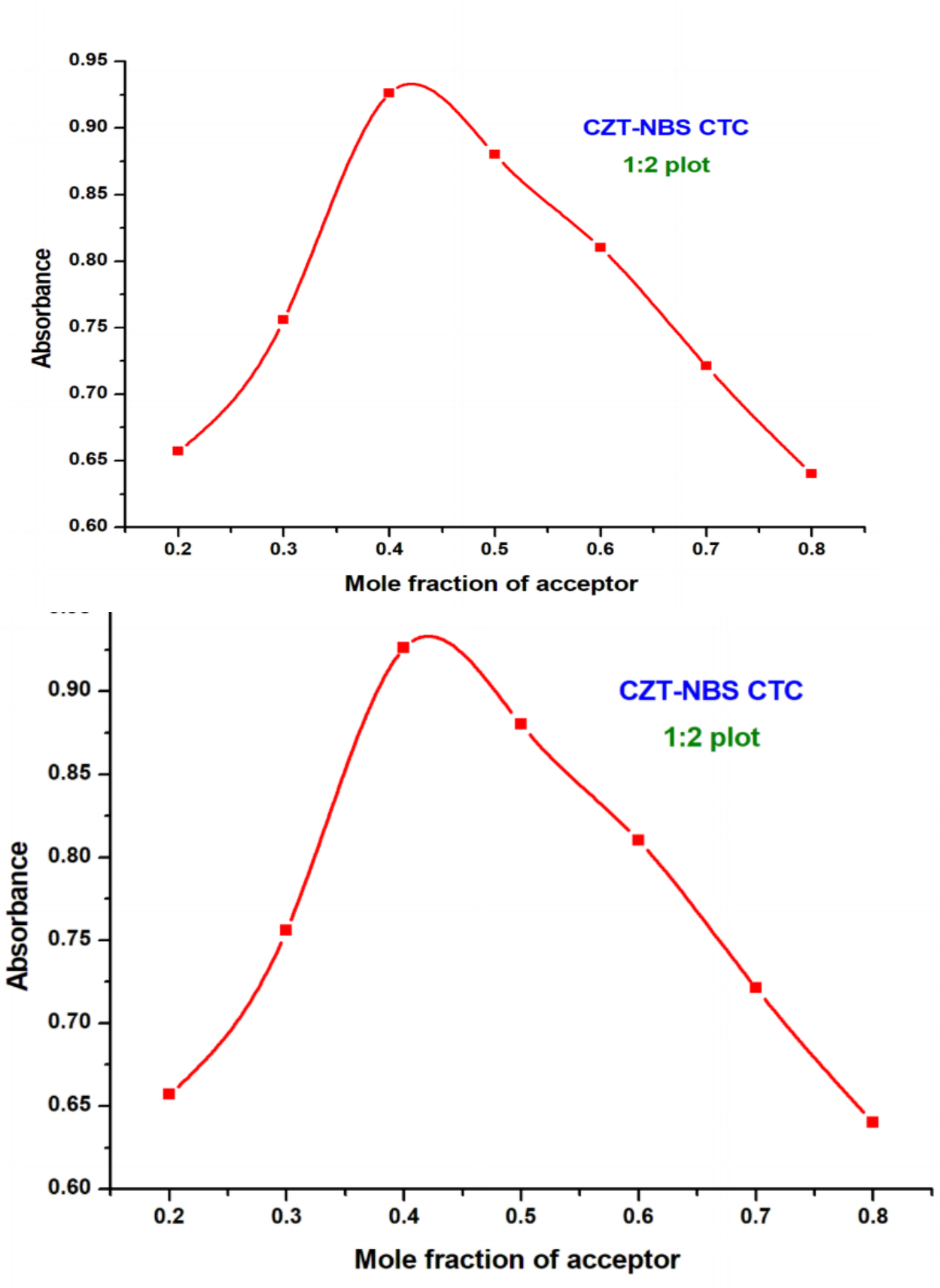
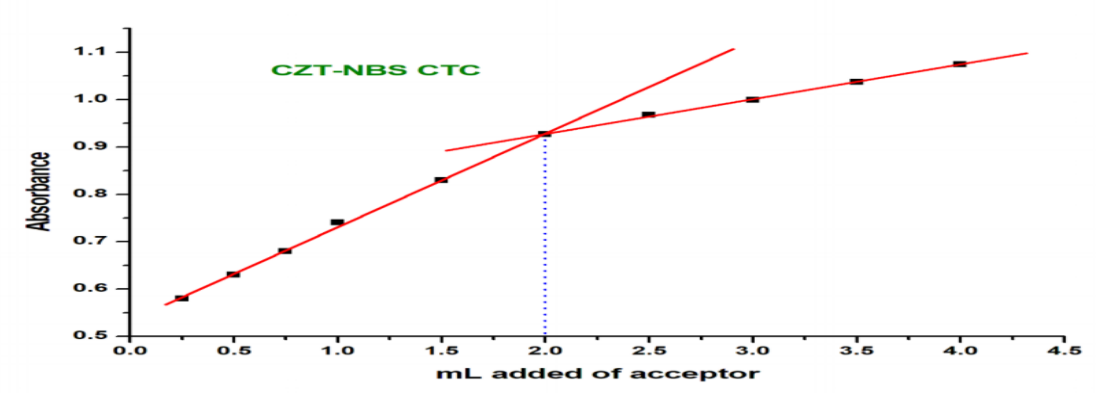


Fig. 3. Jobs plot of the CZT-NBS CTC ($5x10^{-4}$ M)



4.5. Association constant of CZT-NBS CT complex

Representative Benesi–Hildebrand plot is shown in (**Fig.5**) and the values of both K and ε are thus determined and are compiled in (**Table-2**) along with the other spectroscopic parameters data. In general, the 1:2 complexes exhibit high association constant values (K), accordingly, the CZT-NBS complex shown higher K value. This high K value indicates a strong interaction between the CZT and NBS.

High association constant value which was obtained by Benesi–Hildebrand 1:2 equation, suggest the good binding affinity between n-*d*onor CZT and acceptor NBS. The high association constant values are common in *n*-electron donors, where the intermolecular overlap may be considerable[10].

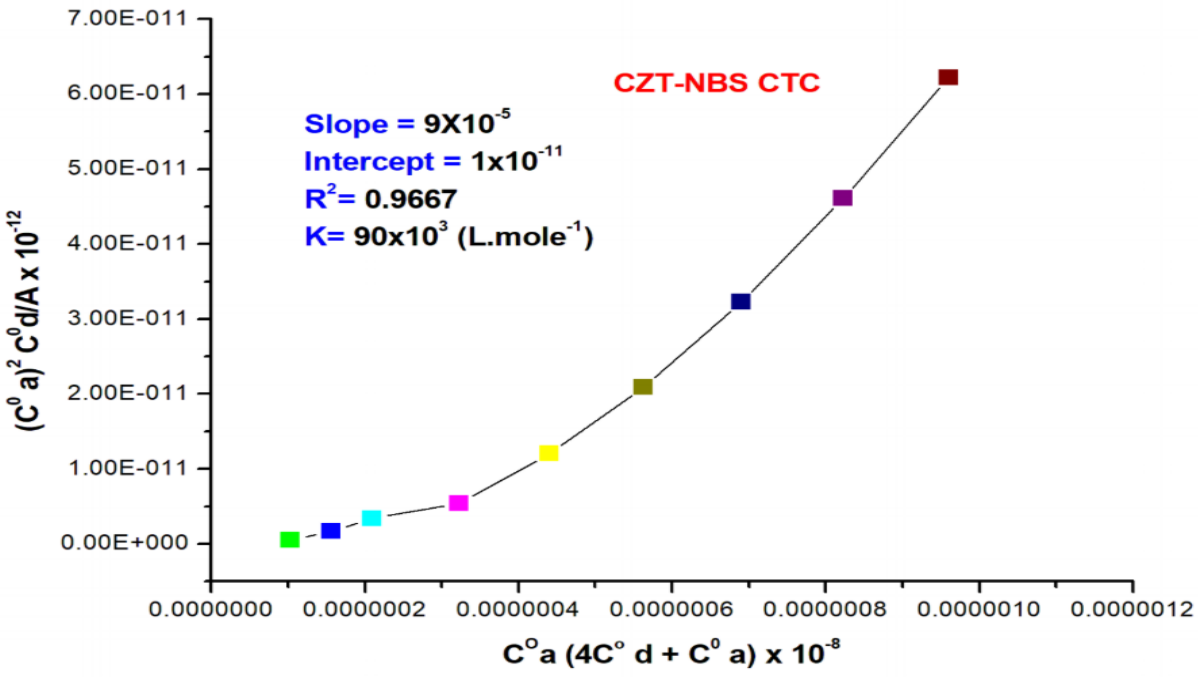


Fig. 5. The 1:2 Benesi–Hildebrand plot for CZT-NBS CTC

5. Calculation of spectroscopic Parameters

In order to support the formation and nature of CZT-NBS CT complex, spectroscopic parameters like, Ionization potential (IP), Energy of the charge transfer complexes (E_{CT}), Resonance Energy (R_N), Dissociation energy (*W)* and Standard free energy changes (ΔG^0) of the CT Complexes were calculated.

5.1. Ionization Potential (IP)

The ionization potential (IP) of the highest filled molecular orbital of the donor was estimated from CT energies of its complexes with the acceptor making use of the following empirical Aloisi and Pignataro equation[11]. The calculated IP values for molecular orbital participating in CT interaction of the donors are compiled in the **Table -2.**

$$\mathbf{h\nu_{CT} = a\ IP^D + b}$$

Where, a = 0.87 and *b* = − 3.6, $h\nu_{CT}$ is the energy of CT complex. 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.

5.2. Energy of the charge transfer complexes ($h\nu_{CT}$*)*

The energy ($h\nu_{CT}$) of the CT Complexes were calculated using the following equation[12] and the values are compiled in the **Table -2**.

$$\mathbf{h\nu_{CT} = 1243.667/\ \lambda_{CT}\ (nm)}$$

Where, λ_{CT} is the wavelength of the complexation band.

5.3. Resonance Energy (R_N*)*

Resonance Energy (R_N) of CT Complexes were determined by the following theoretically derived equation by Briegleb and Czekalla[13] and the values were compiled in the **Table -2**.

$$\mathbf{\varepsilon_{max} = 7.7\ X\ 10^{-4} / [h\nu_{CT} / [R_N] - 3.5]}$$

Where, ε_{max} is the molar absorptivity of the CTC at maximum charge transfer band, ν_{CT} is the frequency of the CT peak and R_N is the resonance energy of the complex in the ground state, which is obviously a contributing factor to the stability constant of the complex.

5.4. Dissociation energy (W)

Further evidence of the nature of CT interaction in the present CT complexes is the calculation of the dissociation energy (*W*) of the CT excited state of the complex. The dissociation energy (*W*) of the formed CT complex was calculated from the corresponding CT energy (E_{CT}), ionization potential of the donor (IP) and electron affinity of the acceptor (EA) using the following relationship[14] and the calculated values of *W* are compiled in (**Table -2**.)

$$h\nu_{CT} = IP - EA - W$$

Where, $h\nu_{CT}$ is the energy of CT complex, IP is the ionization potential of the donor and EA is the electron affinity of the acceptor.

5.5. Standard free energy changes (ΔG^0)

To add more conformation for the nature of CT interaction, standard free energy change values (ΔG^0) were calculated and are compiled in **Table-2**, the higher negative values suggest that the CT complexes formed between β-AB and I_2 are exothermic. Generally, the values of ΔG^0 become more negative as the value of K increases where the CT interactions between the donor and acceptor become strong. Thus, the components (donor and acceptor) are subjected to more physical strain or loss of degree of freedom and the values of $\Delta \mathbf{G^0}$ become more negative[15].

The standard free energy changes of complexation (ΔG^0) were calculated from the association constant values by the following equation.

$$\Delta G^0 = - RT \ln K$$

Where, ΔG^0 is the free energy change of the CT Complexes ($KJmol^{-1}$), R is the gas constant ($1.987 calmol^{-1}K^{-1}$), T is the temperature in Kelvin and K is the association constant of the CT Complexes at room temperature.

Table - 2. Spectroscopic parameters of the CZT-NBS CT Complex

	CZT-NBS
Wavelength: λ_{max} (nm)	280
Extinction coefficient: ε_{max} (L mole $^{-1}$ cm $^{-1}$)	$11x10^3$
Association constant: K (L $mole^{-1}$)	90 $x10^3$
Energy: $h\nu_{CT}$ (eV)	4.416
Ionization Potential: IP (eV)	9.2432
Resonance Energy: R_N (eV))	1.261
Dissociation energy : *W (eV)*	2.2716
Gibbs free energy: ΔG^0 ($KJmol^{-1}$)	$-6.755x10^3$

The calculated spectroscopic parameters values like Energy of the CT complex ($h\nu_{CT}$), Ionization Potential (IP), Resonance Energy (R_N), Dissociation energy (*W)* and Standard Gibbs free energy (ΔG^0*)* suggests that the investigated CZT-NBS complex was reasonably strong and stable under the studied conditions.

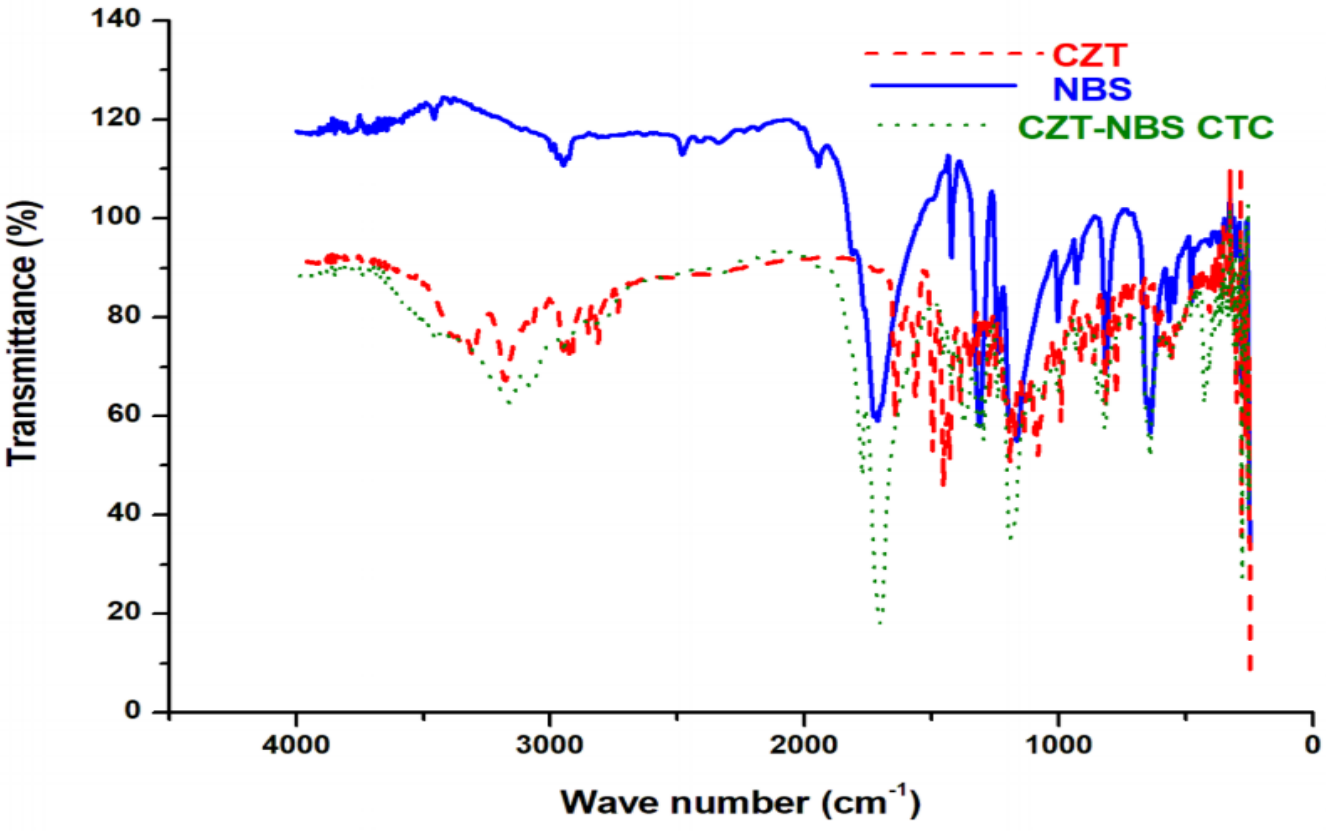
The association constant is strongly dependent on the nature of the acceptor used including the type of electron withdrawing substituents to it such as bromo and carbonyl groups of NBS (acceptor). The association constant value is equal to 90 $x10^3$ L/mol (Table-2), that reflects the relatively higher electron acceptance ability for NBS. The number of donating atoms available in the donor is another important factor that affects the stability of charge transfer complexes [16]. High association constant value (Table-2) of CZT-NBS suggests the strong interaction between CZT

(donor) and NBS (acceptor) Since in the process of molecular complexation, it is reasonably assumed that the charge density is donated from the donor to acceptor, the increased number of nitrogens in the donor (CZT) is expected to increase the donor acceptor interaction in solution. The effective overlapping of donor-acceptor orbitals involves the proper spatial positions of donor and acceptor molecules. This also needs specific conformation of donor. During complexation, some energy is consumed for the conversion of most stable conformation of free donor to a conformation which is suitable for complex formation.

6. Spectral Characterization

6.1. FT-IR spectroscopy

FT-IR spectroscopy is extensively used in organic chemistry for the identification of functional groups of organic compounds as well as the studies on molecular conformation, reaction kinetics, etc., Assignment for complex systems can be propounded on the basis of frequency agreement between the computed harmonics and the observed fundamentals. Therefore, FT-IR spectra of the CZT, NBS and their respective CTC (CZT–NBS) were measured in the range of 4000–250 cm^{-1}.



The FT-IR spectra of three are shown in **Fig. 5**. A comparison of the relevant infrared spectral bands of the CZT free donor and NBS acceptor and their respective CTC (CZT-NBS) clearly indicate that the characteristic bands of CZT show some shift in the frequencies (**Table-3**), as well as some change in their band intensities. This could be attributed to the expected symmetry and electronic structure changes upon the formation of the charge transfer complex, which Suggest that the CT complex is formed through *n*-π* charge migration from HOMO of the donor to the

LUMO of the acceptor. It is noteworthy to say that the spectra of CZT-NBS complex have a sharp broadening with distortion in the stretching vibration bands.

The frequency of N-H bands, ν (N-H) which were 3379.29 cm^{-1}, 3305.99 cm^{-1} (CZT) before the complexation are shifted to 3458.37 cm^{-1}, 3300.05 cm^{-1} (CZT-NBS) after the complexation, ν (C-H) which were 2956 cm^{-1}, 29142 cm^{-1}, 2849 cm^{-1} (CZT) before the complexation are shifted to 3077 cm^{-1}, 2848 cm^{-1}, 2791 cm^{-1}, 2953 cm^{-1} (CZT-NBS) after the complexation, Aromatic Hydrogens which were 3023 cm^{-1}, 3066 cm^{-1} ,3083 cm^{-1} (CZT) before the complexation are shifted to 3021 cm^{-1}, 3077 cm^{-1}, 3078 cm^{-1} (CZT-NBS) after the complexation, ν (C=O) which was 1673 cm^{-1} (NBS) before the complexation is shifted to 1777 cm^{-1} (CZT-NBS) after the complexation. Moreover, there is a slight change in frequency values of the remaining functional groups, which clearly suggest the CT from CZT to NBS.

Table-3. Important Infrared absorption frequencies (cm^{-1}) and tentative assignments of CZT and CZT–NBS CT complex

CZT	NBS	CZT-NBS	Assignments
3379.29, 3305.99	3079, 3052	3458.37, 3300.05	ν (N-H)
2956, 29142, 2849, 773.46	2925, 2869, 2854	3077, 2848, 2791, 2953	ν (C-H)
-	775.50		ν (C-Cl)
1388.75	-	1369.46	ν (C-CH_3)
1273.02	-	1242.16	ν (C-F)
3023,3066,3083	-	3021, 3077, 3078	Aromatic hydrogens
1080.14	-	1068.56	ν (C-O-C)
1496.76, 1564.27		1458, 1531	C=N- (conjugated, cyclic)

1673

1777,1703 ν (C=O), ν (C=C)

7. Conclusion

The CT reaction of CZT as electron donor and NBS as electron acceptor has been studied for the first time. The study includes the use of spectrophotometry in the comprehensive manner. A single solvent DMSO has been used to avoid solvent interactions with CZT (donor) and NBS (acceptor). The FT-IR is used to characterize the formed complex between CZT and NBS. Spectral data acquired from spectral analysis has suggested that CZT acted as an electron donor when interacted with NBS (π - acceptor). Hence, the biological activity of CZT may be due its donating ability as is evident from the association constant (K) and standard Gibbs free energy (ΔG^0) values. The spectroscopic parameters like Ionization Potential (IP), Energy of the complex, $h\nu_{CT}$ (eV), and Resonance Energy (R_N) values also support the strong interaction of CZT with NBS. Therefore, the mechanism for the interaction of the studied CZT is useful in understanding the binding of this bioactive molecule under real pharmacokinetic conditions, which enables medical fraternity to pay attention towards the importance of this novel drug, which may potentially contribute to the knowledge in the medicinal field.

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