ADDIS ABABA UNIVERISTY
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COMPARISION OF DONATION STRENGTH OF PRIMARY AMIDES WITH TCP USING ASSOCIATION CONSTANT BY FTIR SPECTROPHOTOMETER

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COMPARISION OF DONATION STRENGTH OF PRIMARY AMIDES WITH TCP USING ASSOCIATION CONSTANT BY FTIR SPECTROPHOTOMETER

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This is to certify that the thesis prepared by Amin Abdullahi Gelchu, entitled: ‘‘comparison of donation strength of primary amides with TCP using association constant by FTIR spectrophotometer” and submitted in partial fulfillment of the requirements of the Degree of Master of Science in Chemistry (Physical Chemistry) compiles with regulation of the University and meets the accepted standards with respect to originality and quality.

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ABSTRACT

Comparison of donation strength of primary amides with TCP using association constant by FTIR spectrophotometer

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Addis Ababa University, 2018

The study of amides structure is fundamental for modeling and predicting the behavior of larger molecules, such as proteins which plays essential roles in biological processes, functioning as structural supporters, catalysts and so on. Charge-transfer complexes are associations of donor (electron-rich) molecules with acceptor (electron-deficient) molecules which exhibit absorption. The charge-transfer complexes of the donor of some primary amides with the acceptor 2, 4, 6-tricholorophenol (TCP) studied by infrared spectroscopy in acetonitrile at room temperature. Equal masses of (1:1) donor (amides) and acceptor (TCP) solutions were prepared for FTIR analysis. The results indicate that the formation of a CT complex are depend on a substituent attached to amide functional group that more electron donating group comparatively high association constant. The physical parameters of the CT complex were evaluated by the Benesi–Hildebrand equation and results are discussed in terms of the formation constant, molar extinction coefficient and standard free energy. The comparison of the formation constant of the amide complex indicates that (K_{CT}) formed was dependent upon the nature of the electron donor.

Keywords: Donor, Acceptor, Charge transfer, complexes, Formation constant, FTIR

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List of Abbreviations

IR	Infrared
CT	Charge transfer
B-H	Benesi- Hildebrand
TCP	2,4,6-Trichlorophenol
ACT	Acetamide
PROP	Propionamide
PIC	Picolinamide
NIC	Nicotinamide
QM	Quantum Mechanics
DFT	Density functional theory
B3LYP	Becke3-parameters; Lee, Yang, and Parr correlation
GTO	Gaussian type orbital
STO	Slater type orbital
HF	Hartree-Fock

1. INTRODUCTION

A charge-transfer complex (CT complex) is a complex that is formed by weak association of molecules or molecular subgroups, which one molecule or molecular subgroup acts as an electron donor and the second molecule or molecular subgroup acts as an electron acceptor. The association of charge-transfer complex does not establish a strong covalent bond; the nature of the attraction in a charge-transfer complex is not a stable chemical bond [4, 6].

The term charge-transfer complex, introduced firstly by Mulliken in the early fifties, has opened to the development of the first quantum mechanical theory of these complexes. Mulliken assumed that a 1:1 complex would have a wavefunction that could be expanded in terms of a set of basic functions of the donor and acceptor molecules. In dilute solution, the stoichiometry A: D of these complexes remains as 1:1 at a large excess of the donor concentration. At a higher concentration of the acceptor, with a small excess of donor, it is possible to form CT complexes with other stoichiometries. Structures of 1:1 charge transfer complexes have been intensely investigated by both experiments and simulations. The Mulliken theory of charge transfer complexes also leads to relationships between thermodynamic and spectroscopic properties of the complex [5, 9].

Charge transfer complex is a special class of molecular complexes which have attracted the attention of chemists, biologists, physicists and scientists of other disciplines and it is a fundamental importance in nature. Due to its wide applications and consequences, charge transfer complexes were studied extensively in various fields like solar cells, molecular electronics, nonlinear optics, sensors and analytical estimation of drugs [8, 14].

The charge-transfer association occurs in a chemical equilibrium with the independent donor (D) and acceptor (A) molecules.

$$D + A \rightleftharpoons DA$$

In terms of quantum mechanics, this is described as a resonance between the non-bonded state (D.A) and the dative state (D^+–A^-) and this expressed by an approximate wavefunction

$$\psi_N(DA) = \underbrace{a\psi_0(D.A)}_{\text{no-bond}} + \underbrace{b\psi_1(D^+ - A^-)}_{\text{dative}}.$$

The intensity of charge-transfer bands in the absorbance spectrum is strongly dependent upon the degree (equilibrium constant) of this association reaction. The equilibrium constant of the complexes in solution is determined by measuring the intensity of absorption bands as a function of the concentration of donor and acceptor components in solution. Mulliken's suggests that, an increase in the equilibrium constant, *K*, should be accompanied by an increase in the intensity of the charge transfer band**.** Later studies have shown that the stability of the complex decreases with increasing intensity of the charge transfer band in different solvents.

The characterization of the charge transfer complexes was carried out by several measurements including determination of association constant (K_{CT}) and molar extinction coefficient (ε). The values of association constants that characterize charge transfer complex are strongly dependent on the nature of the donor and acceptor used in the charge transfer complexation.

There are spectroscopic and non-spectroscopic methods that have been developed independently to study the charge transfer complexes. The non-spectroscopic methods for the evaluation of the equilibrium constants were reviewed more than forty-five years ago. Now spectroscopic methods are generally used to study the charge transfer complexes in solution, solid state and gas phase. There is disagreement between values of equilibrium constants of charge transfer complexes determined by different methods.

The equilibrium constant of charge transfer complexes in vapour phase are markedly different from the corresponding values in solution. Although these results clearly suggest strong solvent participation in the equilibrium, direct comparison of the results in vapour phase and solution is difficult due to both, lack of consistency/uniformity in vapour phase measurements and also the interactions between solvent and solute which affects the free associations of the complex components, thus considerably changing the intensity of the absorption.

Research on charge transfer complexation originated in 1949 with the observation by Benesi and Hildebrand of a new absorption band in the solution that does not appear in the spectrum of either alone. However, absence of new bands does not rule out the formation of charge transfer complexes, particularly for very weak charge transfer complexes in which such changes are not very pronounced [23].

2. THEORETICAL ASPECTS

2.1. Infrared spectroscopy

Infrared is a part of the electromagnetic spectrum between the visible and microwave regions. Infrared spectroscopy is used to gather information about the structure of a compound and as an analytical tool to assess the purity of a compound. The IR region is divided into three regions: the near, mid, and far IR. The mid IR region is of greatest practical use to study the fundamental vibrations and associated rotational vibrational structure. This is the region of wavenumber between 4000 cm^{-1} – 400 cm^{-1}. Near and far IR is regions of IR with wavenumber between 12820-4000 cm^{-1} and 400-33 cm^{-1} respectively. Far-IR has low energy and may be used for rotational spectroscopy and Near-IR can excite overtone or harmonic vibrations.

Infrared radiation is absorbed by organic molecules and converted into energy of molecular vibration. In IR spectroscopy, an organic molecule is exposed to infrared radiation. When the radiant energy matches the energy of a specific molecular vibration, chemical bonds vibrate (stretch and bend) and absorption occurs. Absorptions of radiation in the infrared region are quantized and appear as sharp line. However, each vibrational transition within the molecule is associated with rotational energy changes and thus appears as combination of vibrational-rotational bands.

The vibrational frequency of a bond has dependent on force constant and effective mass. According to Hook's law, frequency of vibration is given as

$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$ and reduced mass is given by $$\mu = \frac{m_1 m_2}{m_1 + m_2}.$$

Where c, μ, K and $\tilde{\nu}$ are the velocity of light in vacuum, effective mass, force constant and vibrational frequency respectively.

The above equation implies vibrational frequency is directly related to force constant or bond strength and inversely related to effective mass. The vibrational frequencies of double bond are higher than single bond within the same atoms and the lower reduced mass has higher vibrational frequencies. Stretching absorption of band is also higher frequency than bending, which means the stretching absorption of a band always appear at higher energy than the bending absorption of the same band.

2.2. Amides

Amides are the simplest molecules containing a peptic linkage. The studying of amides structure is fundamental for modeling and predicting the behavior of larger molecules, such as proteins which plays essential roles in biological processes, functioning as structural supporters, catalysts and so on. In addition amides are interesting functional compounds which play great role in organic synthesis and pharmaceutical industries.

Amides can be classified as primary, secondary and tertiary amides based on the number of substitutions on nitrogen atom. The IR studies of amide give a fundamental absorptions and N-H stretch is observed in the range of 3475-3150 cm^{-1}. Primary amides show two bands near 3350 cm^{-1} and 3180cm^{-1}, secondary amides show only one band around 3300 cm^{-1}. N-H bending also occurs around 1640-1550 cm^{-1}. Tertiary amides will show only C=O in the range of 1680-1630 cm^{-1}, but will not show an N-H stretch.

Primary amides have two major bands in IR spectrum. The first major band is carbonyl band and the second major band is N-H bands. The wavenumber of carbonyl amide bond is usually below 1700 cm^{-1} because of lone pair electron on amide nitrogen is conjugated with carbonyl bond and C-N bond has a partial double bond nature, thus lowers the stretching frequencies of amide band.

The existence of amide complex formation using infrared spectroscopy was first studied by Gramstad and Funglevic and later by Schmulbach and Hert with phenol as acceptor. The hydrogen-bonded complexes of amide with phenol were studied by Leroux using mid and near IR spectroscopy. The study of hydrogen bonding has wide applications to understanding the nature of protein structure.

2.3. Charge transfer complexes

Charge-transfer complexes are associations of donor (electron-rich) molecules with acceptor (electron-deficient) molecules which correspond to an electronic transition in which electron density is transferred from the donor molecule to the acceptor molecule. It has been studied extensively over the last century to understand the mechanism for stabilization of many chemical and biological structures [7, 25].

The charge-transfer interactions have received a great deal of attention in recent years. The first attempt to explain the charge-transfer complex on the basis of theoretical considerations was made by Robert S. Mulliken based on the valence-bond treatment of the charge transfer complexes. Since then, a number of theoretical modifications to his original theory have been proposed but the theory is still useful in discussing the properties of charge transfer complexes. Mulliken's theory refers only to the systems in the gaseous phase, whereas most of the data available today are for condensed states where considerable polarization interactions and environmental effects on the given pair of molecules of a complex have to be considered. For a solid state, Kroll assumed even $\infty:\infty$ stoichiometry for complexes is possible. But, for crystalline complexes, it is very difficult to apply a mulliken theory because of solid state complexes contain infinite molecular stacks. The thermodynamic complex formation can be extended to DA crystals, but it is then difficult to determine the various polarizations, CT and other processes relating the energy of the solid to that of isolated donor and acceptor molecules [11,19,25].

Modern theoretical approaches to explain the formation of charge transfer complexes proposed by Mulliken that a valence-bond theory of charge transfer complexes based on diatomic molecules which share a pair of electrons to form a covalent bond. The resonance structures of charge transfer complexes could be written in term of electron donors (D) and acceptors as the following,

$$D + A \rightleftharpoons \underset{\substack{\text{nobond}\\ \text{structure}}}{D.A} \rightleftharpoons \underbrace{D^{+} - A^{-}}_{\substack{\text{dative}\\ \text{structure}}}$$

The dative structure is formed by transfer of an electron from the highest occupied molecular orbital (HOMO) of the donor molecule to the lowest unoccupied molecular orbital (LUMO) of the acceptor. The wave function for the charge transfer complex in its ground state and excited state of 1:1complexes between D and A could be written as

$$\Psi_N (DA) = a\psi_0 (D.A) + b\psi_1 (D^+\text{-}A^-) \text{ and}$$

$$\Psi_E (DA) = a^* \psi_1 (D^+\text{-}A^-) + b^* \psi_0 (D.A)$$

respectively where *a*, *b* are coefficients for the wavefunction that represent the contribution of the 'no-bond' and 'dative' structures to the overall wave function ψ_N respectively and *a** and *b** are the contributions of the dative bond and no-bond states to ψ_E respectively. $\Psi_N (DA)$ is total wave function of complex between A and D, $\psi_0 (D.A)$ is no-bond wave function and $\psi_1 (D^+\text{-}A^-)$ is dative wave function [1, 7, 9, 11, 16, 20].

For weakly bound charge transfer complexes, b is equivalent to the amount of charge transferred from D to A and the value is determined from the relationship between electronic structures and spring constant K in terms of overlap integral S_{01} in equation

$$(K_0 - K_N) / K_0 = 1 - (K_1 / K_0) (b^2 + abS_{01})$$

where K_0 and K_1 are the wavenumber force constants in ground state and excited state respectively, K_N is the force constant for the bond in the CT complex.
If ψ_N, ψ_0 and ψ_1 are normalized, so that

$$\int \psi^2_N \, d\tau = 1, \int \psi^2_0 \, d\tau = 1 \text{and} \int \psi^2_1 \, d\tau = 1$$

The coefficients '*a*' and '*b*' are the constants related by the expression:

$$a^2 + 2abS_{01} + b^2 = 1$$

Where $S_{01} = \int \psi_0 \psi_1 d\tau$ and the overlap integral S_{01} is zero. Thus, gives $a^2 + b^2 = 1$ and $a^{*2} + b^{*2} = 1$.

The charge-transfer transition $\psi_N \rightarrow \psi_E$ is essentially involves the jump of one of a pair of electrons initially occupying a molecular orbital in donor to an unoccupied molecular orbital in acceptor. These N→E spectra may be called intermolecular charge-transfer spectra. They constitute a generalization of the familiar intense interatomic charge-transfer spectra of molecules. Then it may be shown that

$$S_{01} = \sqrt{2}\, S_{AD} (1 + S^2_{AD})^{1/2}$$

where $S_{AD} = \int \psi_A \cdot \psi_D \, d\tau$, the overlap integral between the highest filled molecular orbital of the donor and the lowest unfilled molecular orbital of the acceptor. Usually S_{AD} is very small and hence S_{01} varies with S_{AD}. Thus the charge-transfer transition involves a ground state and an excited state with very different dipole moments. The bond energies of formation of charge-transfer complexes are less than the bond energies associated with common chemical bonds [1, 15, 24].

The study of the charge-transfer processes may be divided into four general areas, such as theoretical aspects, inorganic systems, organic systems and biological systems. Among those, charge-transfer for organic systems is the focus of this work.

2.3.1. Organic charge-transfer complexes

Organic charge-transfer complexes are intensively studied because of their special type of interaction, which is accompanied by transfer of an electron from the donor to the acceptor and also protonation of donor from acidic acceptor. Organic charge transfer complexes have been known since the beginning of twentieth century as addition products obtained from the stable compounds. Sudborough in 1901 suggested that these addition compounds were held together with covalent bonds. However, Pfeiffer in 1927 believed that the bonding in a compounds occurred through the saturation of residual valences in the component molecules. These ideas were opposed by Bennet and Wain because of no explanations of stoichiometries could be given based on the above theories. Also the instantaneous attainment of equilibrium in solution opposed the concept of covalent bonding in these systems [12, 25].

The modern developments in the area of organic CT complexes began in 1949 after Benesi and Hildebrand reported that new electronic absorption bands were found when the solutions of iodine in non-polar solvents were mixed with different aromatic hydrocarbons. This band was not present in either of the two components taken separately. These observations led Mulliken to interpret these new bands in terms of intermolecular charge transfer transitions [1, 12].

2.3.2. Classification of Organic Charge-Transfer Complexes

Organic charge-transfer complexes have been classified on the basis of the type of molecular orbitals of electron donors and acceptors which take part in the formation of intermolecular bonds. The donors and acceptors are classified according to their structure and function. These classifications can be outlined as follows.

1. R-type donors: Such donors are radicals containing odd-number of electrons. Free radicals such as DPPH (Diphenylpicry hydrazyl) fall into this category.
2. n-type donors: The molecules containing lone-pair of electrons are called n-type of donors. They contain even number of electrons. Such donors are amines, alcohols, ketones, aldehydes etc.
3. π-type donors: The molecules containing π-electrons are called π-donors. They contain even number of electrons in their highest occupied π-orbital. Such donors are aromatics, olefins, acetylenes etc.
4. σ-type donors: The molecules in which sigma-bonding electron pairs take part in the formation of the charge transfer complexes are called σ-donors. These molecules form much weaker complexes. They also contain even number of electrons.

Similarly electron acceptors have been classified as the following,

1. Q-type acceptors: The molecules containing odd-number of electrons i.e. having radical character categorized in Q-type acceptors.
2. V-type acceptors: The lowest molecular orbital is completely vacant. For example, BF_3, metal halides etc.
3. π-type acceptors: The molecules in which the transferred electron goes into the vacant anti-bonding molecular orbitals are called π-acceptors. The examples of such acceptors are tetracyanoethylene, tetracyanoquinine etc.

4. σ-type acceptors: The molecules in which charge transfer is affected by the occupation of the lowest vacant anti-bonding σ-molecular orbitals are called σ-type acceptors. The examples are halogens particularly molecular iodine which forms a variety of charge transfer complexes from some of the strongest to the weakest.

Based on donor-acceptor pairs, the charge transfer complexes have been classified as (I) R-Q, (II) n-π, (III) n-σ, (IV) π-π, (V) π-σ, (VI) n-v, (VII) π-v, (VIII) σ-v etc. In principle, any donor can interact with any acceptor, the interaction being determined by the thermodynamics of the same process. Also the same molecule can behave either as a donor or as the acceptor depending on its partner. Another interesting aspect of charge transfer complexes is that the same basic moiety could be used as a donor or acceptor depending on the substituents [21, 22].

2.3.3. Equilibrium studies

Equilibrium constant of charge transfer complexes can range from zero, which implies no complex formation, to infinity, which implies complete conversion of stoichiometric quantities of the donor and the acceptor into the complex. The complexes with formation constants less than unity are classified as weak, while for strong complexes the formation constant is greater than unity.

In 1949, however, Benesi and Hildebrand reported a graphical method for the simultaneous evaluation of the formation constant, K, and the molar extinction coefficient, ε, of 1:l EDA complexes formed between some aromatic hydrocarbons (acting as electron donors) and iodine (an electron acceptor) in inert solvents like carbon tetrachloride and heptane.

The Benesi- Hildebrand equation takes the form:

$$\frac{[A]_0}{A} = \frac{1}{K\varepsilon_\lambda} \cdot \frac{1}{[D]_0} + \frac{1}{\varepsilon_\lambda}$$

where $[A]_0$ is the initial concentration of the acceptor and is kept constant throughout, $[D]_0$ is initial concentration of the donor and is varied and always kept in large excess over the acceptor, K is the association constant, and ε is the molar absorptivity and A is the absorbance of the complex at wavelength λ.

A plot of $[A]_0/A$ with $1/[D]_0$ is linear with the intercept equal to $1/\varepsilon_\lambda$ and the slope equal to $1/K\varepsilon_\lambda$. The estimation of *K* by this method leads to the separation of *K* and ε_λ. However, the *K* cannot appear single and the value of *K* depends on molar extinction coefficient to evaluated accurately [1].

The applications of Benesi-Hildebrand are in order and the value of equilibrium constant of charge transfer is unaltered if D and A are switched. Nearly many researchers are employed the condition [D] >> [A] because most of electron acceptors have low solubility in the solvents employed. So the Benesi-Hildebrand equation also takes the form

$$\frac{[D]_0}{A} = \frac{1}{K\varepsilon_\lambda} \cdot \frac{1}{[A]_0} + \frac{1}{\varepsilon_\lambda}$$

Benesi-Hildebrand equation is derived from the equilibrium between the donor and acceptor with CT complex

$$D + A = DA$$

The equilibrium constant K is given by

$$K = \frac{[DA]}{[D][A]}$$

where, $[D]_0$ is the initial concentration or the total concentration (complexed and uncomplexed) of donor, [D] + [DA] and $[A]_0$ is the initial concentration of acceptor given by [A] + [DA].
Then, [D] and [A] is equal to $[D] = [D]_0 - [DA]$ and $[A] = [A]_0 - [DA]$.
Substituting in to equation (1) gives

$$K = \frac{[DA]}{\{[D]_0 - [DA]\}\{[A]_0 - [DA]\}}$$

If $[D]_0$ is much greater than $[A]_0$, $\{[D]_0 - [DA]\} \approx [D]_0$. So equation (2) becomes

$$K = \frac{[DA]}{[D]_0\{[A]_0 - [DA]\}}$$

Rearranging the equation (3) becomes

$$[DA] = \frac{K[D]_0[A]_0}{1 + K[D]_0}$$

According to Beer's law, CT complex absorbance by [DA] is given by

$$A = \varepsilon l[DA] = \varepsilon l\left(\frac{K[D]_0[A]_0}{1 + K[D]_0}\right)$$

Rearranging equation (5) gives the Benesi-Hildebrand equation

$$\frac{[A]_0}{A} = \frac{1}{K\varepsilon}\frac{1}{[D]_0} + \frac{1}{\varepsilon}$$

The equilibrium constants for the formation of charge transfer complexes determined by spectrophotometric measurements. The most common method for the measurement of equilibrium constants of charge transfer complexes involves a study of the UV-Visible absorption spectrum of the complex [11].

The study of the Benesi-Hildebrand tells that most of the equilibrium studies are based on the assumption that the stoichiometry of the complex is 1:1 only. However, not much attention has been paid to the possible existence of complexes with stoichiometry other than 1:1[1].

Most of the complex in nature is weak and studied in limited concentration range because at very high concentration may complicate a measurements due to solute-solvent and solute-solute interactions. The interaction of solvent with both donor and acceptor decrease the association constant than the correct association constant.

2.3.2.1. Methods for determination of association constant

There are spectroscopic and non-spectroscopic methods for the determination of charge transfer complexes. But, non-spectroscopic methods are time consuming and laborious with little practical value. So, the spectroscopic methods are well to determine the formation of CT complex. The spectrophotometer, especially the computerized one is easy to operate and from the absorbance, association constant can be evaluated easily by using a Benesi-Hildebrand type of equation.

Association constant of charge transfer complex are mostly determined by UV-Visible spectrophotometric technique due to simplicity, accuracy and availability of appropriate graphical and linear methods.

Besides the UV-Visible spectrophotometric technique, many other methods of evaluating the formation constants of charge transfer complexes have been developed over the years and the principles of these methods have been reviewed by Foster:

1. Infra-red spectroscopy, using the same principles as UV-Visible spectrophotometry;
2. Nuclear magnetic resonance spectroscopy; from the change in the chemical shifts leading to a relationship similar to Benesi-Hildebrand's;
3. Polarography, by measuring the shift in the half-wave potential as the donor is added to the solution of the acceptor;
4. Calorimetry, which allows simultaneous measurements of the formation constant as well as the heat of formation of the complex;
5. Dielectric constant measurements for determining the formation constants of hydrogen-bonded complexes;
6. Distribution methods, partitioning one of the components of the complex between two immiscible liquids;
7. In the case of reactive charge-transfer complexes, from the rates of their reaction following their (nearly instantaneous) formation in equilibrium;
8. Refractometry and
9. Conductometry methods.

2.3.2.2 Infrared studies of charge transfer complexes

Infrared spectroscopic method is one of the typical methods for determination of small molecules. This standing is due to its sensitivity to the chemical composition and structure of molecules as well as the range of the spectrum peak observed is wide and the bands of IR spectrum are not overlapping as UV-Vis spectrophotometer, but the studies of charge transfer complexes in Infrared spectroscopic are rare [25].

Vibrational spectra of CT complexes have been the subject of recent reviews. Foster has surveyed the spectra of individual complexes and Mulliken and Person have discussed the theoretical background. The general theory of vibrational spectra of complex is first introduced by Ferguson and Matsen, and then generalized by Friedrich and Person [4, 15, 18, 25].

In the infrared spectra, the spectra of charge-transfer complexes formed from donor and acceptor and the spectra of those of the isolated molecules (donor and acceptor) which form the complexes, there are three types of properties are established to ensure the formation of charge transfer complexes.

1. The vibrational frequencies in donor or acceptor (or both) may be shifted.
2. The intensities of the bands may be changed considerably, and
3. New low-frequency bands appear due to the vibrations of one molecule in the complex against the other or intermolecular vibrations.

In a strong complex a fourth change might also occur: this is the appearances of one or more new bands due to the symmetry change of the molecular environment upon complex formation.

In the first time, vibrational frequency shift of charge transfer complex is observed in Benzene and chlorine molecule system ($b\pi$-$a\sigma$). In pyridine-XY complexes (n-$a\sigma$), (where X and Y are halogen atoms), the larger shifts have been observed and intermolecular vibrational bands have also been observed in such complexes.

In the case of 1:1 π- π complexes, three π- π systems have been broadly studied in Infra-red spectroscopy: nitro aromatic with aromatic amine complexes, the Hexamethylbenzene with Tetracynoethylene complex and quinone with hydroquinone complexes. In these complexes, a new low frequency bands and the appearances of one or more new bands are not observed. Lutskii have carried out the most extensive study on nitro aromatic-aromatic amine complexes with 16 solid complexes of aromatic and heterocyclic amines with picric acid, 1,3,5-trinitrobenzene and 2,4,6-trinitroanisole to determine the respective roles of -OH and $-NO_2$ groups in complex [9, 11, 15, 25].

2.4. Density functional theory calculations

Quantum mechanics is a mathematical description that can predict the property of an individual atom or molecule exactly. A mathematical formulation of QM was formulated by Schrödinger equation;

$$\hat{H}\psi = E\psi$$

where $\hat{H}$ is the Hamiltonian (Energy) operator, ψ is a wavefunction and E is the energy.
Quantum chemical calculations are broadly classified into two classes. These are *ab-initio* methods and semi-empirical calculations. Ab-initio methods also include hartree Fock (HF) and density functional theory. For this work, all theoretical (computational) calculations were performed using density functional theory [31,32].

Density functional theory is the most popular method in current years that justified based on accurate observations that it is less computationally than other method. In DFT the energy of the molecule can be determined from the electron density. It originated with a theorem by Hoenberg and Kohn, that theorem applied only to finding the ground state electronic energy of the molecule. The electron density is expressed as a linear combination of basis functions similar in mathematical form to hartree-fock orbitals. The advantage of using electron density is that the integral of columbic repulsion done only over the electron density, which is three dimensional functions and some energy correlations, can be included in these calculations [32].

Density functional theory (DFT) calculation use basis sets weather DFT-optimized or typical HF-optimized basis sets. The studies using DFT-optimized have shown little and most DFT calculations todays are being done with typical HF-optimized GTO basis sets. DFT calculations also use numerical integrals. Calculations using GTO basis sets are not faster than those using other types of basis sets. STO basis sets or numeric basis sets would be more accurate due to the correct representation of the nuclear cusp and exponential decay at long distances [32].

B3LYP hybrid functional was the most widely used for molecular calculations. This is due to the accuracy that obtained for a large range of compound particularly organic molecule. This hybrid functional is combination of Becke's empirical exchange functional with empirical correlation functional of Lee, Yang and Parr [32].

3. OBJECTIVES

3.1. General objective

The general objective of this study is to compare donating strength of primary amides with 2, 4, 6-trichlorophenol (TCP) using association constant parameter by FT-IR.

3.2. Specific objectives

- Determine the association constant of some primary amides by using infrared spectrophotometer.
- Compare association constant of some primary amides.
- Determine the standard free energy from association constant.
- Calculate standard free energy computationally.
- Compare qualitatively the experimental results with DFT calculations.

4. EXPERIMENTAL PART

4.1. Materials and Chemicals

Acetamide (98%, BDH Limited Pole, England), Propionamide (98%, AlfaAesar, Germany), Picolinamide (98%, AlfaAldrich, Japan), Nicotinamide (BDH, laboratory reagent, England), 2,4,6-trichloro-phenol (97%, Merck KGaA, Germany), Distilled water and Acetone (99.9%, Sigma-Aldrich, Switzerland) were used as cleaning agents. All the above chemicals were studied without further purifications.

For this work, the instruments used are PerkinElmer 65 FTIR spectrophotometer, Attenuated total reflection (ZnSe), Chem-Draw ultra 8.0 software and Gaussian 09 view software used for density functional theory.

4.2. Methods and Procedure

IR spectra of the charge transfer complex were recorded with PerkinElmer spectrum 65 FTIR Spectrophotometer. The spectral resolutions were $1cm^{-1}$and 4 scans. Their FTIR spectra were recorded in the range of 400–4000 cm^{-1} at standard temperature.

A 0.01M acetamide, propionamide, picolinamide and nicotinamide were prepared in acetonitrile as a solvent. The different concentration of 2,4,6-trichloro-phenol (0.002M, 0.003M, 0.004M and 0.005M) also prepared by dissolving in acetonitrile as a solvent. Then, 3 ml of the amides and TCP were added and the total volume of mixture was prepared for infrared spectroscopic analysis. Then, a liquid IR samples were run at room temperature and IR spectra of different mixtures were recorded.

From IR spectra, association constant are determined using Benesi-Hildebrand equation and standard free energy change is calculated from association constant. Then, the experimental results are compared qualitatively with DFT calculations.

5. RESULTS AND DISCUSSION

5.1. Infra-red spectra of primary amides with 2, 4, 6-Trichlorophenol

The charge transfer complexes between the primary amides and 2, 4, 6-Trichlorophenol (TCP) formed as indicated from the infrared spectra of TCP, amides and their mixtures (complex) in acetonitrile solvent which given below. The donation process from the donor (amide) to acceptor (TCP) can occur from either electron density in nitrogen atoms of amino group or carbonyl oxygen of amides. The CT complex forming reactions of amides (especially for alkyl amides) with TCP are based on the concept that n-donor react with σ-acceptor to form a CT complex.

From infrared spectrum, the intensity change at a different concentration of TCP with acetamides is given below.

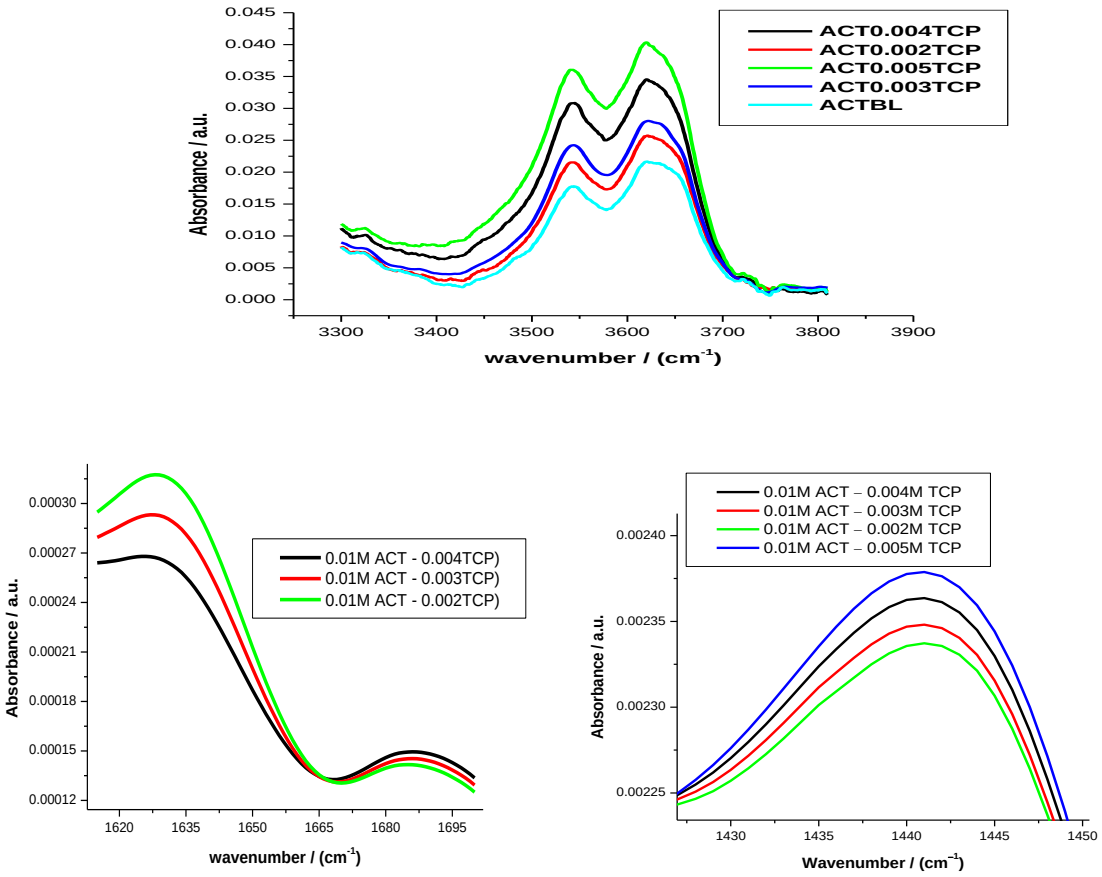


Figure 1: IR spectrum of ACT-TCP complex in acetonitrile

In TCP, the charge deficient part is hydrogen atom of hydroxyl part of phenols. This implies hydroxyl part of phenols is a part which participates in the formation of charge transfer complex. The shift and change of intensity of peak around 1600 cm^{-1} to 1700 cm^{-1} formed between them indicates the interaction between amides and TCP in complex formation. The peak around 1420 cm^{-1} - 1425 cm^{-1} simultaneously decrease as a concentration of TCP increase and the peak appear at around 1440 cm^{-1} - 1445 cm^{-1} increase in intensity as concentration of TCP increase and shifted to lower frequency. Additionally, the intensity change in infrared spectral band between 3450 cm^{-1} to 3650 cm^{-1} show that NH_2 of amides and OH of TCP are participated in the complex formation.

Infra-red spectra of acetamide with TCP implies an increase in the intensity of peak at 1630 cm^{-1} (band I) and simultaneously decrease intensity of peak around 1680 cm^{-1} (band II) as a concentration of TCP increases. This indicates as the amount of TCP increase, electron donating strength of electron donor increased and reduces electron density of carbonyl amide. The band around 3000 cm^{-1} is due to aromatic C-H stretching vibrations. Around 1680 cm^{-1}, TCP doesn't absorb and the intensity change in this area resulted from a weak association between them which is known as charge transfer complexes. Generally, the shift of the frequencies or wavenumbers and change of intensity could be attributed due to the expected symmetry changes upon the formation of charge transfer.

Table 1: Characteristic IR frequencies (cm^{-1}) and assignments for amides, TCP and their charge transfer complex

Amide	**TCP**	**Complex**	**Assignments**
~3622/3542	3620	~3622/3542	$\tilde{\upsilon}(O-H)+\tilde{\upsilon}(N-H)$ N^{+}-H….O^{-}
~1680/1620-1630	1622/1741	1625-30/1665-80	$\tilde{\upsilon}(C=O)$ stretching $\tilde{\upsilon}(C=C)$ aromatic
1370-1450	1442	1370-1450	N-H bending in-plane C-N stretching C-H deformation CH_2 scissoring

From table 1, one can observe that there is the formation of CT complex between amides and TCP. Because there is a frequency shift in addition to intensity change, this frequency shift is one of the characters of a formation of charge transfer complex. In this study, the frequency shift observed mostly in three parts of spectra of amides *i.e.* NH stretching, carbonyl and NH bending. This indicates NH_2 and CO of amides as well as OH of TCP are participated in complex formation.

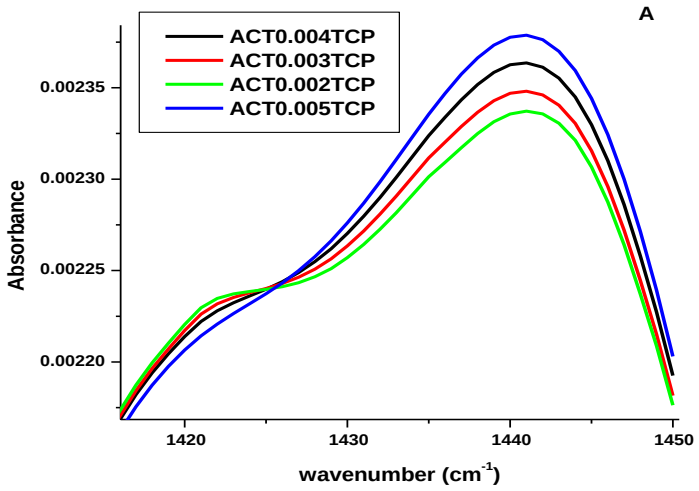
Therefore, based on the experimental observations discussed above, two possible charge transfer complex between primary amides and TCP are determined. This two determined structures are either NH_2 (amino group) of amides with OH (phenolic group) of TCP or CO (carbonyl group) of amides with OH (phenolic group) of TCP.

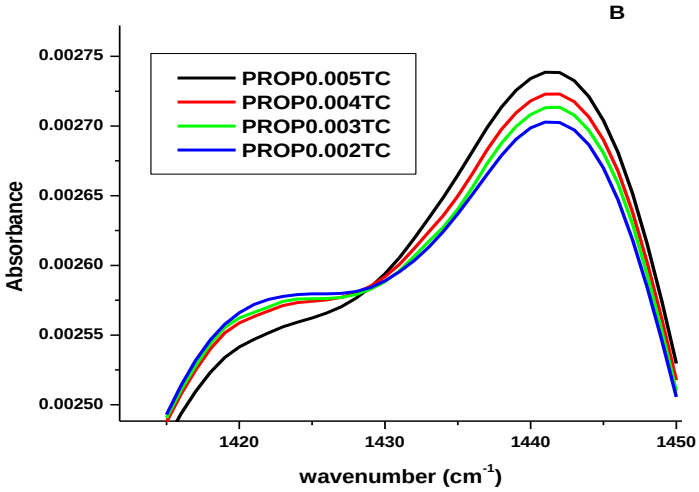
5.2. Spectroscopic Calculation and Thermodynamic Properties of Charge-transfer

5.2.1. Calculation of association constant

For the calculation of association constant, The maximum peak absorbance values of the complex (the complex of different concentrations of the TCP and the concentration of the primary amides in this work) are used to determine the value of association (charge transfer) constant K_{CT} by using Benesi-Hildebrand equation.

The spectra of all amides which imply complex formation with acceptor TCP are given below.





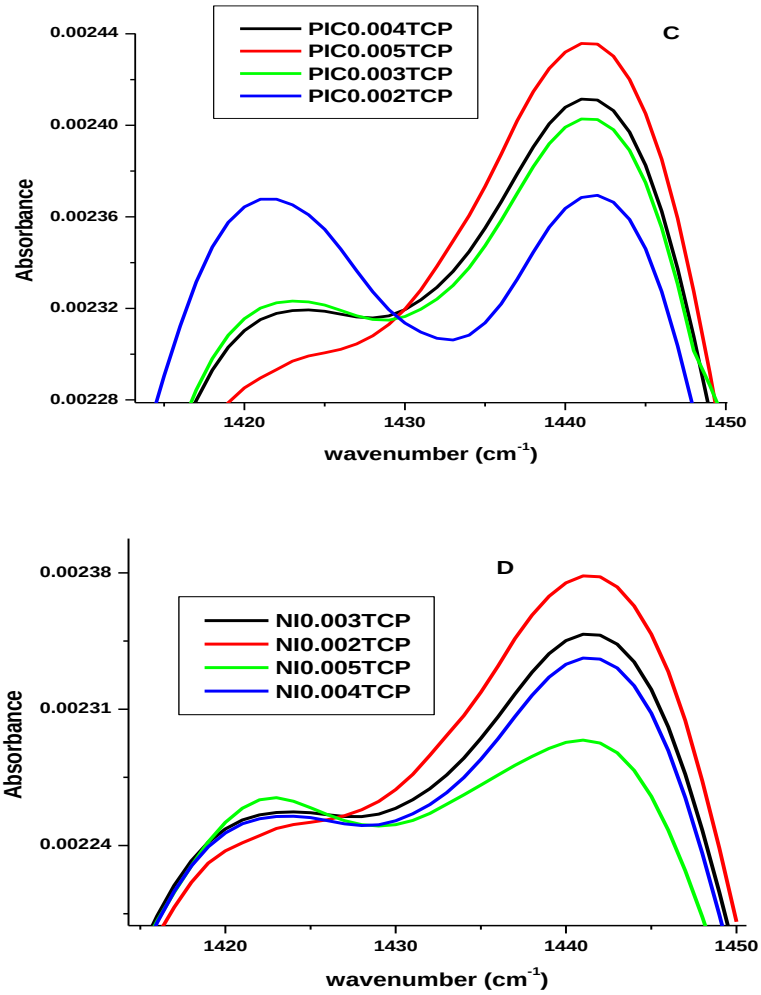


Figure 2: Concentration dependence of IR Spectra of: A) ACT-TCP B) PROP-TCP C) PIC-TCP D) NIC-TCP

Table 2: Maximum absorbance of different concentration of all amide-TCP complexes

Concentration of Acceptor	Absorbance			
	Propionamide	Acetamide	Picolinamide	Nicotinamide
0.002M	0.0027010	0.002335	0.002369	0.0022941
0.003M	0.0027172	0.002350	0.0024075	0.0023363
0.004M	0.0027250	0.002366	0.0024115	0.00234852
0.005M	0.0027360	0.002378	0.0024358	0.0023785

From the Benesi-Hildebrand equation, the equilibrium constant of charge transfer complex between some primary amides and common acceptor (TCP) are determined with a plot of $[D]_0$ /A with 1/ $[A]_0$ where 1/Kε and 1/ε are slope and Y-intercept respectively.

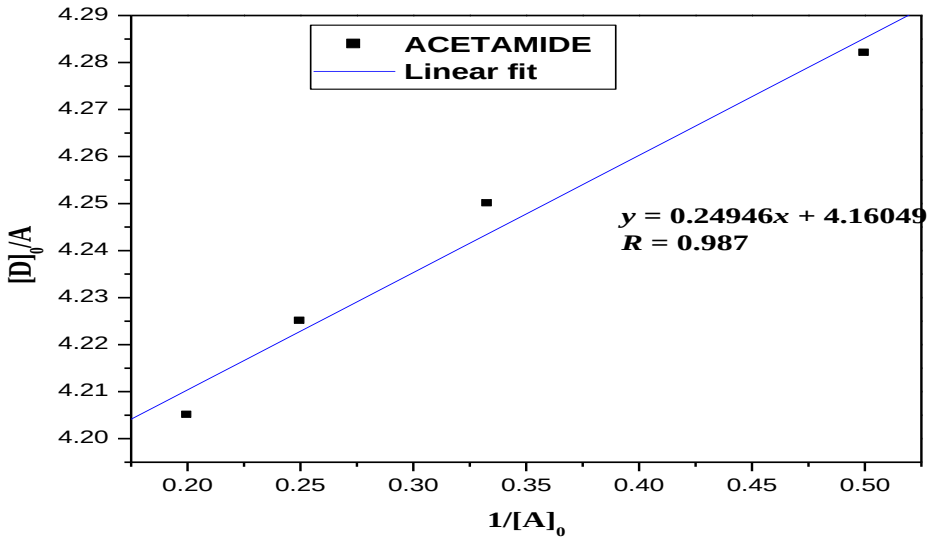


Figure 3a: Relation between [D]/A and 1/[A] in B-H equation of ACT with TCP

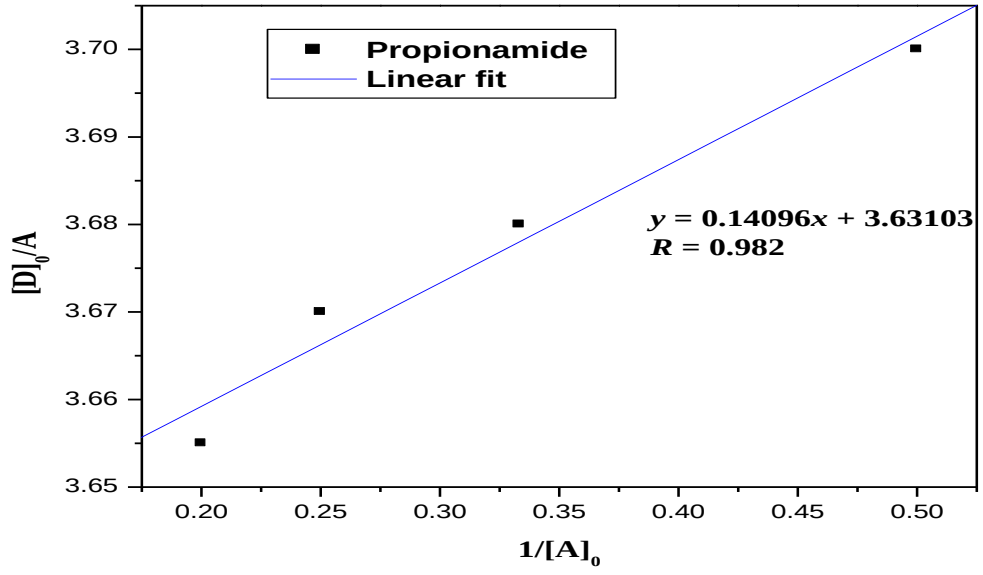


Figure 3b: Relation between [D]/A and 1/[A] in B-H equation of PROP with TCP

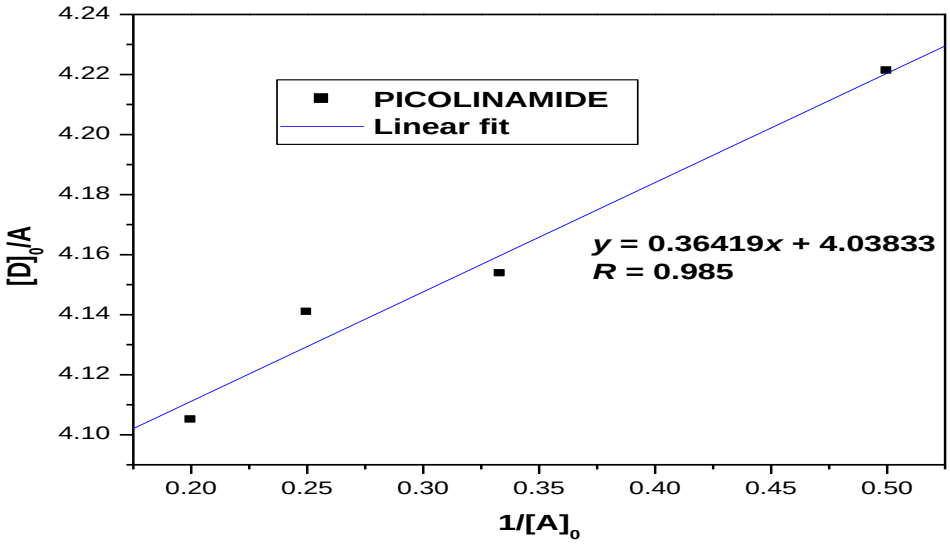


Figure 3c: Relation between [D]/A and 1/[A] in B-H equation of PIC with TCP

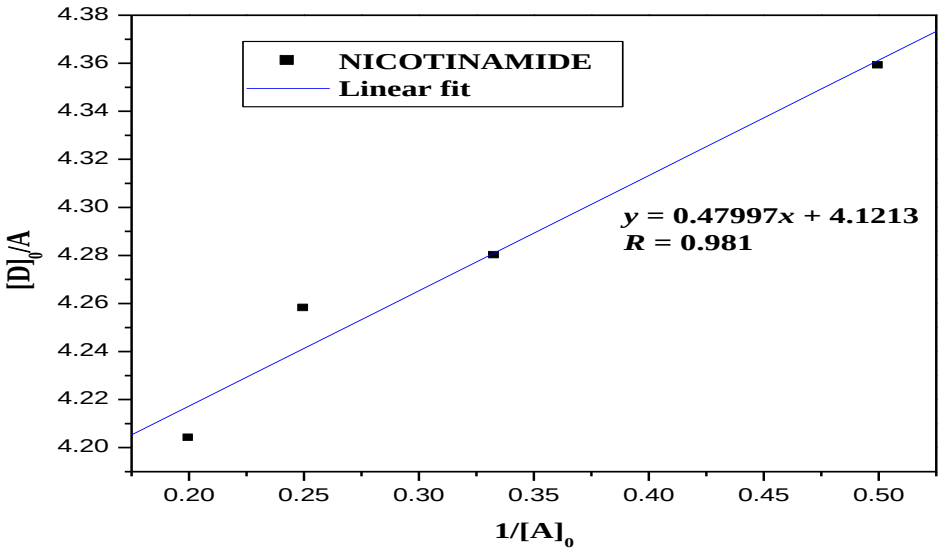


Figure 3d: Relation between [D]/A and 1/[A] in B-H equation of NIC with TCP

From the figure above, one can observe that the graph of the donor concentration with the maximum absorbance and the inverse of the concentration of acceptor (TCP) give a linear fit. By using the B-H equation the values of slope and y-intercept indicated the charge transfer complex constant and the molar absorptivity coefficient of 0.01M of acetamide with 0.002M-0.005M of TCP are 1.6678×10^{-3} and 2.403×10^{-2} respectively. The value of K_{CT} indicates the formation of charge transfer complex between acetamide and TCP; this confirmed that the regression line is almost nearest to one (0.987).

In the table below (Table 2) association constant and molar absorptivity coefficient value of different amides with TCP charge transfer complex are summarized.

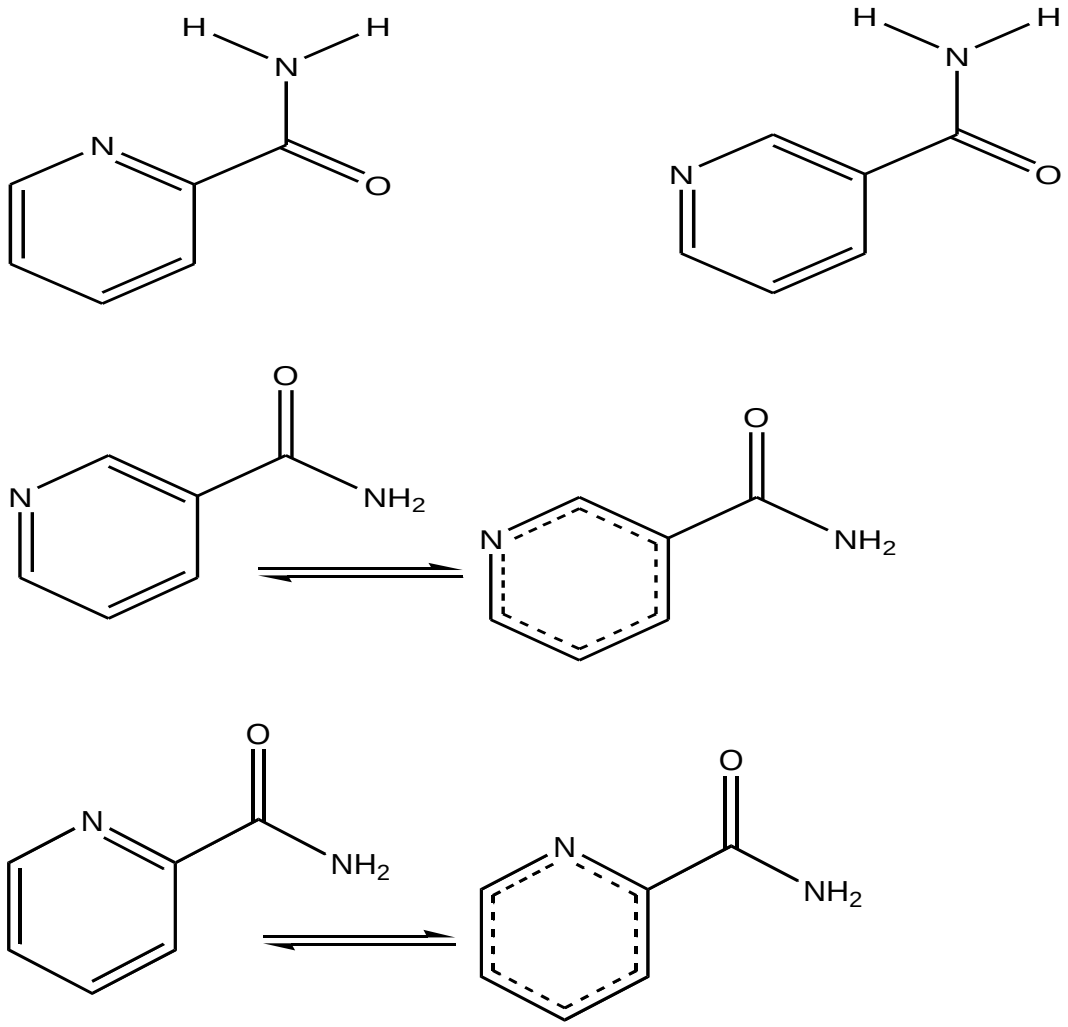
Table 3: The value of association constant and molar absorptivity coefficient of different amides

Amides	**K_{CT} (m^3mol^{-1})**	**ε (m^2mol^{-1})**
Nicotinamide	0.8587×10^{-3}	2.426×10^{-2}
Picolinamide	1.1088×10^{-3}	2.476×10^{-2}
Acetamide	1.6678×10^{-3}	2.403×10^{-2}
Propionamide	2.576×10^{-3}	2.754×10^{-2}

From table 2, one can observe that the K_{CT} value of all amides with TCP indicates the formation of charge transfer complex between donor amides and acceptor of TCP molecule. The experimental values of charge transfer constant of different amides with common acceptor have slightly different. The variation in association constant value of the formation of charge transfer complex depends on the donating strength (electronic density factor) of substituted group (methyl, nitrogen atom of aromatic ring) in amide functional group, simply the nature of donor.

Contrary to the expectation based on common understanding, the alkyl groups are found to possess more electron donating property than the pyridnyl groups. This could be attributed to induction effect which may isolate the electron cloud from the surrounding chemical environment, and consequently decreasing the donating strength. Accordingly, propionamide and acetamide demonstrated a considerably higher electron donor capacity than nicotinamide and picolinamide, which can be confirmed by the higher association constants observed for propionamide and acetamide than nicotinamide and picolinamide.

Generally, in analogous series, the alkyl group charge donating capacity increases with increase in number of carbon atoms. Expectedly, a higher charge transfer constant is observed for propionamide compared to that of acetamide. Usually, a larger value of K_{CT} indicates a greater stability of charge transfer complex, and therefore, propionamide forms a more stable complex with TCP than acetamide as well as all the remaining amides.



Scheme 1: The structure of nicotinamide, picolinamide and their resonance structure

In the case of nicotinamide and picolinamide, the position of nitrogen atom in benzene ring is also having an effect on K_{CT} value. For nicotinamide, there is a resonance between nitrogen of aromatic ring and amide functional group, most probably, resulting in the formation partial positive charge on the nitrogen atom of pyridine and partial negative charge in carbon that substituted in amide functional group.

The positive charge on the meta-position conjugates with the carbon atom of pyridine, which is connected to the amide moiety, consequently decreasing the charge donor capacity of nicotinamide. Due to this very fact, nicotinamide revealed the smallest association constant of all the four amides investigated.

Additionally, for picolinamide, there is a formation of hydrogen bonding between the ortho-nitrogen of pyridnyl groups and hydrogen of nitrogen in amide functional group and the bond strength between amide nitrogen and hydrogen is decrease, which increases the electron density (donating strength) of nitrogen atom of amide. The formation of hydrogen bond in nicotinamide (meta-nitrogen) is less than picolinamide. Therefore, the association constant of picolinamide is greater than nicotinamide.

5.2.2. Calculation of Change of free energy

The value of K_{CT} calculated from experimental result is used to determine the standard Gibbs free energy (ΔG^o) of the charge transfer complexes by equation:

$$\Delta G^\circ = -RT \ln K_{CT}$$

where, R and T are molar gas constant and thermodynamic temperature respectively. The calculated standard free energy gained from association constant is given in table 3.

Table 4: Change of Gibbs free energy of amide experimentally

Amide	Nicotinamide	Picolinamide	Acetamide	Propionamide
ΔG^o (KJ/mol)	-5.33	-5.96	-6.97	-8.05

The changes of Gibbs free energy value of all amides show that the complex is thermodynamically favored. The free energy change of the complex also tells that the CT complex formation between the amides and TCP are exothermic in nature and spontaneous. The value change of Gibbs free energy goes to more negative value as the association constant of the complex is increase. Generally, from Gibbs free energy one can concluded that the complex of propionamide is more stable than acetamide, picolinamide and nicotinamide. The order of stability of complex formation of four amides in these studies is: Propionamide > Acetamide > Picolinamide > Nicotinamide

5.3. DFT result

The most probable structure from the suggested structures of charge transfer complexes is determined by DFT methods calculation with 6-31G (d,p) basis sets in geometry optimization and frequency calculation to get change of free energy for charge transfer complexes. The DFT results of free energy is used to the qualitative comparison of experimental result and determine the stability of a formation of charge transfer complex.

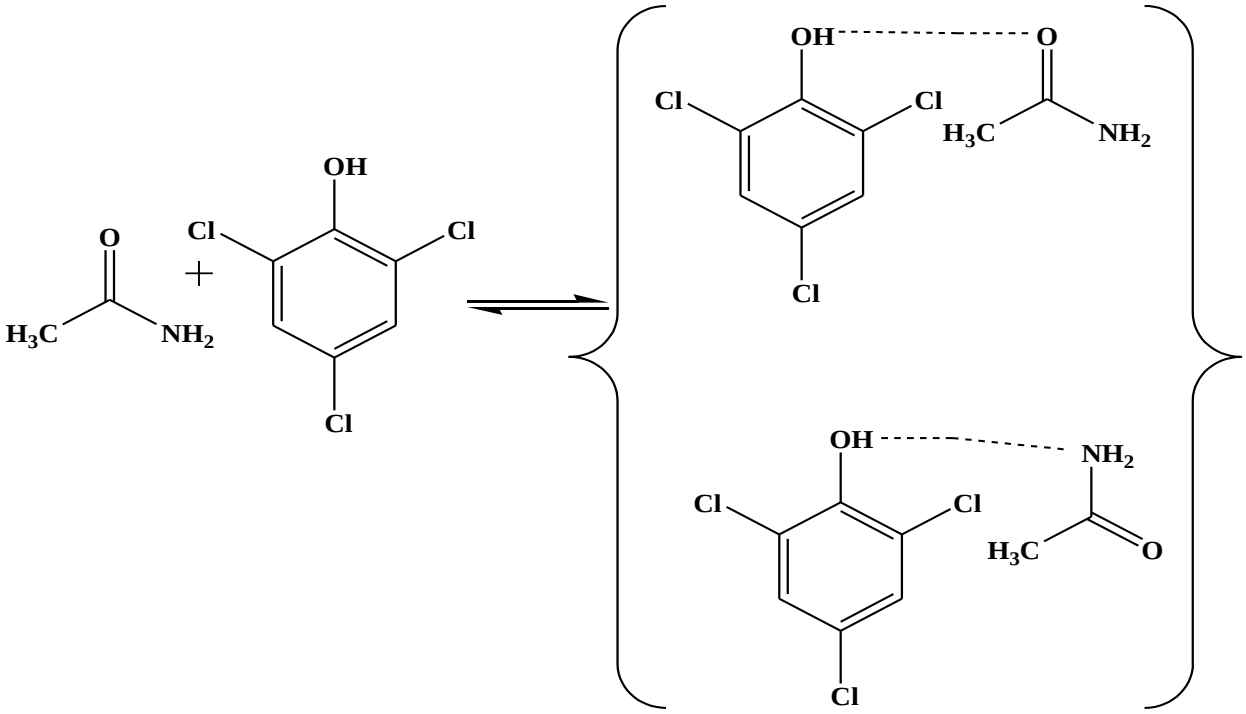
From DFT result, the change of free energy of complexes with N····H and O····H binding site are given in table below.

Table 5: The computed free energies of the two proposed CTCs of ACT-TCP in acetonitrile

	Acetamide	
	N····H	O····H
Gibbs free energy	-67220 $Jmol^{-1}$	-67210 $Jmol^{-1}$

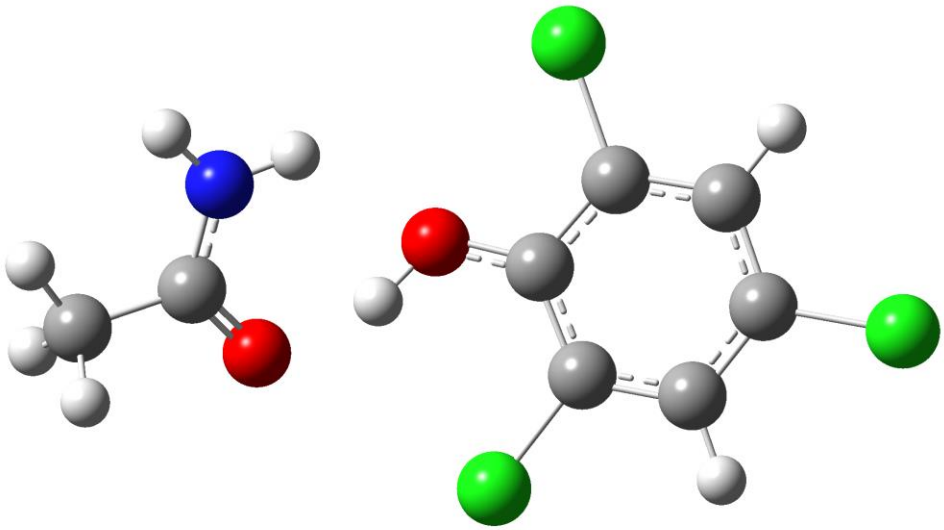
The change in free energies of acetamide with the binding site of carbonyl is fairly smaller than (-67210 $Jmol^{-1}$) that of the binding site of amino nitrogen (-67220 $Jmol^{-1}$). This implies amino nitrogen binding site are stable for the formation of charge transfer complex. The difference in change of free energies between two binding site is -10 $Jmol^{-1}$.

The two suggested structure of complexes of acetamide with TCP (both nitrogen of amide functional group with hydrogen of hydroxyl phenol and oxygen of carbonyl amide with hydrogen of hydroxyl phenol which is supported by both experimental and theoretical calculation) are seen below.



Scheme 2: The two proposed interactions between acetamide and TCPH

The structures of all amide-TCP complexes are determined using DFT and a linear relationship between experimental and DFT result of free energies are given below.



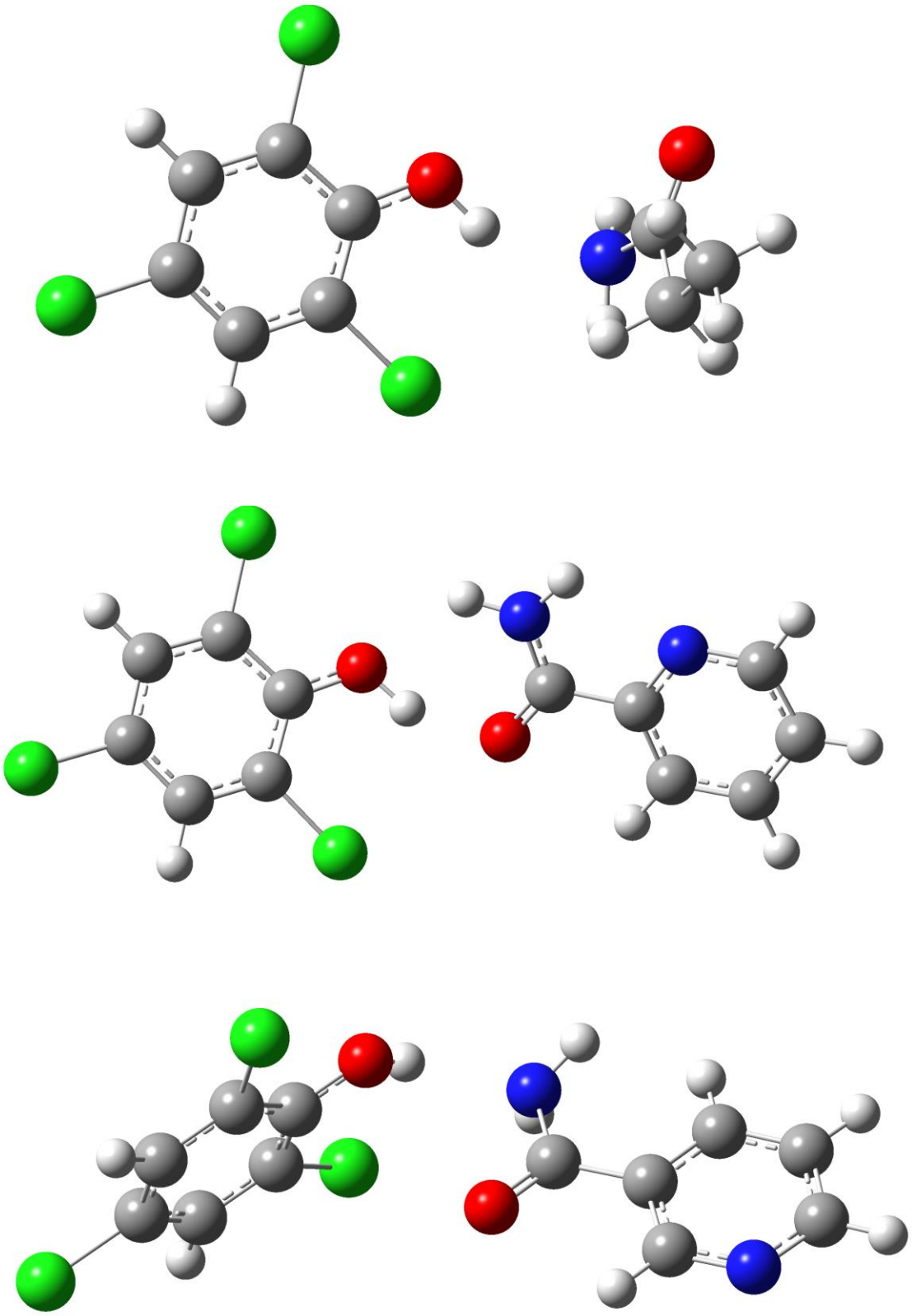


Figure 4: the structure of CT complex of all amides-TCP complexes from DFT calculation

Table 6: The experimental and DFT result of standard Gibbs free energy in $KJmol^{-1}$

Amide	Experimental	DFT
Nicotinamide	-5.33	-29.00
Picolinamide	-5.96	-37.00
Acetamide	-6.97	-40.00
Propionamide	-8.05	-54.29

From the above table, the plot of experimental change of free energies with theoretical (DFT) change of free energies is given in figure 4.

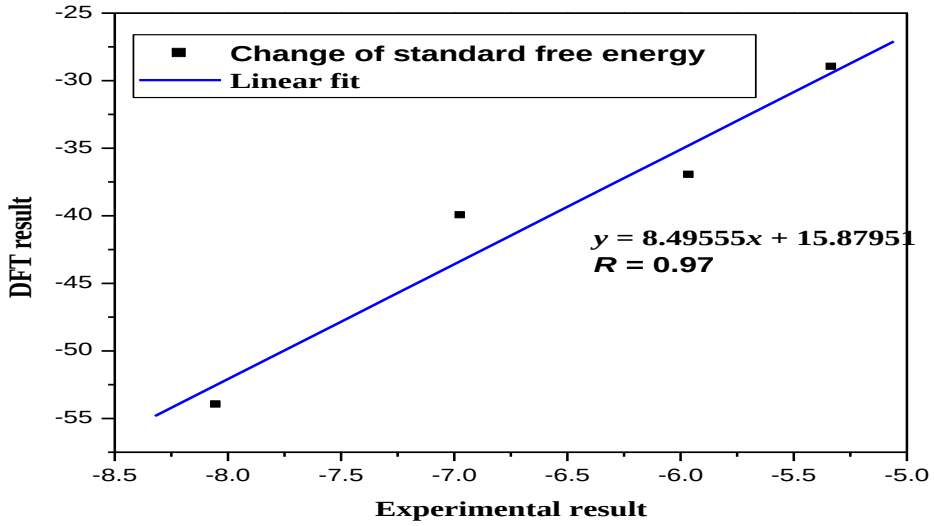


Figure 5: Relation between experimental and DFT result of Gibbs free energy

From above table, a plot of change of free energies of experimental calculated from association constants with DFT calculations of a complex give a linear fit. From both results, anyone can conclude that, the experimental and DFT results are feasible and qualitatively good agreement. From the linear fit of experimental and DFT calculations of free energy, the validity of both results has been observed and the validity of the linear fit is cross checked with the R (0.97) value.

6. CONCLUSION

Charge transfer complex formation of four primary amides was investigated using infrared spectrophotometer. The spectra of the amides in acetonitrile with 2,4,6-trichlorophenol as an acceptor molecule revealed the formation of a 1:1 acceptor-donor complex formation. The strength of the formed charge-transfer complexes was evaluated based on the association constants. The thermodynamic parameters calculated from K_{CT}, indicated that the charge-transfer complexes were thermodynamically stable and the formation is spontaneous. Further, computational results were used to theoretically support the experimental findings as well as to propose the most probable structure of charge transfer complex.

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