PHOTOPHYSICAL PROPERTIES OF SOME HETERO-AROMATIC AND CARBONYL COMPOUNDS

BY

ADEOYE, MORIAM DASOLA
B. Sc. Chemistry (OAU), PGDE, M. Sc. Chemistry (Ibadan)
Matric No.: 109414

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ABSTRACT

A large number of hetero-aromatic and carbonyl molecules are useful in pharmaceutical and dye industries. Studies of their transition dipole moment ($\Delta\mu$) and transition polarizability ($\Delta\alpha$) are important because they determine their solubility and usefulness. Experimental determination of these parameters and other electronic properties such as oscillator strength (*f*) using Solvatochromic Shift Equations (SSE) has proved to be unreliable. This is due to the large spread in their reported values and the overlapping of the electronic transition bands for a given molecule. This study was designed to modify the SSE in improving its reliability, and to computationally determine the photophysical properties of some hetero-aromatic and carbonyl compounds with a view to studying the extent of overlap of the electronic transition bands.

The ultra-violet spectra of 2,3-diphenylcyclopropenone; 9,10-phenanthrenequinone; Furan-3,4-dicarboxylic acid; 3,4-diphenylthiophene; 3,4-dicarboxylic-2,5-diphenylthiophene and benzo[b]thiophene in the wavenumber range (25,000 - 52,631) cm^{-1}, in solvents of different polarities at concentrations range of 10^{-6} - 10^{-5} M were measured at 25°C. These compounds were selected for the modified SSE due to the variation in their structures. The magnitudes of *f* in solution (f_s) and in vapour phase (f_v) were calculated using the Onsager-Abe reaction field model equations. The frequencies of electronic transitions in various solvents were used to characterise the observed bands. The SSE was modified by incorporating the molecular ground state polarizability (α), the molar refraction of each compound, Einstein coefficient and stark term. Estimation of the $\Delta\mu$ and $\Delta\alpha$ of these compounds were determined using the modified SSE. The electronic properties: *f*, number of transitions, the frontier orbitals energy gap ($\Delta E_{LUMO-HOMO}$) and associated parameters such as: Ionization Potential (IP) and global hardness (η) of the optimized structures of the molecules were calculated based on Time-Dependent Density Functional Theory using Becke's three parameter with Lee-Yang-Parr modification and 6-31G* basis set.

The spectra of these compounds gave a range of one to five bands designated as S_0-S_1, S_0-S_2, S_0-S_3, S_0-S_4 and S_0-S_5 in order of increasing energy. The magnitudes of f_s and f_v for the observed bands increased with increasing solvent polarities and were within the range 3.2×10^{-4} - 1.78 and 3.1×10^{-4} - 1.33 for hetero-aromatics; 1.4×10^{-3} - 1.52 and 1.3×10^{-3} - 1.23 for carbonyls. Similar trends observed for the experimental values of $\Delta\mu$ and $\Delta\alpha$ indicated that the more a transition is allowed, the greater the probability $\Delta\mu$ being larger than zero. The positive values of $\Delta\mu$ ($5.7\text{x}10^{-3}$ - 1.73D) and $\Delta\alpha$ ($8.0\text{x}10^{-5}$ - 5.5Å^3) for hetero-aromatics; $\Delta\mu$ ($3.7\text{x}10^{-2}$ - 1.23D) and $\Delta\alpha$ ($4.8\text{x}10^{-4}$ - 0.95Å^3) for carbonyls indicated substantial redistribution of the π-electron densities in more polar excited state than the ground state. The $\Delta E_{\text{LUMO-HOMO}}$ were (3.19 - 4.09eV) and (4.36 - 5.43eV) for carbonyls and hetero-aromatics respectively. The IP and η increased as solvent polarity increased, suggesting high stability of these compounds in polar solvents.

The modified equation is better in the estimation of transition dipole moment and transition polarizability. The energy gaps and associated parameters suggested strong activity of the molecules and minimal overlapping of the transition bands.

Keywords: Dipole moment, Energy gap, Solvatochromic shift, Density functional theory, Hetero-aromatic compounds.

Word count: 499

CERTIFICATION

I certify that this study was carried out by Adeoye, Moriam Dasola in the Department of Chemistry, University of Ibadan, Nigeria under our supervision.

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Supervisor	Supervisor
Prof. Idowu Iweibo	Dr Nelson O. Obi-Egbedi
B. Sc. (Ibadan), Ph.D. (Purdue)	B. Sc., M. Sc., Ph.D. (Ibadan)
Department of Chemistry	Senior Lecturer, Department of Chemistry
University of Ibadan, Nigeria	University of Ibadan, Nigeria

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DEDICATION

This work is dedicated to:

The God Almighty

And my late husband, my daughter and mum for their constant love, support and encouragement.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS / SYMBOLS

μ: Dipole moment

α: Molecular polarizability

f: Oscillator strength

$f_{\mathrm{aio(s)}}$: Solution phase Oscillator strength

$f_{\mathrm{aio(v)}}$: Vapour phase Oscillator strength

n: Refractive index

$\Delta\mu$: Transition dipole moment

$\Delta\alpha$: Transition polarizability

EA: Electron affinity

$\boldsymbol{\varepsilon}_{r}$: Dielectric constant

EE: Excitation energy

$|\mu_{ij}|$: Transition momen

M_e: Mass of electron

R: Molar refraction

$\frac{\mu}{r^3}$: Stark term

$\varepsilon_{(v)}$: Molar Absorptivity

v: frequency

K: Einstein coefficient

ω: Electrophilicity index

ɳ: Chemical hardness

IE: Ionization energy

HOMO: Highest Occupied Molecular Orbital

LUMO: Lowest Unoccupied Molecular Orbital

TD-DFT: Time Dependent-Density Functional Theory

B3LYP/6-31G*: Becke’s 1988 3-parameterised hybrid exchange functional and the Lee-Yang-Parr correlation functional, with the orbitals expanded in a 6-31G* basis set

MM: Molecular Mass

DPT: 3,4-diphenylthiophene
DCDPT: 3,4-dicarboxylic-2,3-diphenylthiophene
BT**:** Benzo[b]thiophene
DCF: Furan-3,4-dicarboxylic acid
DPCP: 2,3-diphenylcyclopropenone
PQ: 9,10-phenanthrenequinone

CHAPTER ONE

2.0 INTRODUCTION

The study of molecular systems in the liquid phase is important for understanding a large number of chemical, physical and biological processes. The solvent interactions lead to changes in the molecular solute, affecting its spectroscopic, structural and reactivity properties (Solvato *et al.*, 2002; Raikar *et al.*, 2010). For this reason, the study of solvent effect has been a topic of interest.

Electronic spectroscopy is a powerful tool for better understanding of the structures and properties of molecules (Crammer and Truhlar, 1994; 1996). It can also be used to facilitate the accurate prediction, modification and synthesis of the complex molecular structures (Thomasi and Perisco, 1994; Wen-Ge *et al.*, 2003). The band structures observed in the UV/visible region of the spectra results from changes in energy and electronic charge distributions of molecule due to the electronic transitions from the rotational and vibrational states of one electronic configuration to the rotational and vibrational levels of another when a molecule absorbs or emits quanta of light (Luzhkov and Warshel, 1991). The shifts in the electronic absorption or emission bands of organic molecules induced by solvents are commonly understood as the extent of charge re-organization of solute molecules upon electronic excitation and the excited state deactivation. This is related to the nature of the interaction forces between the bulk solvent molecules, dissolved solute, and the local field created by the solvent cage surrounding the solute molecules (Wen-Ge *et al.*, 2003). It leads to changes in the electrical and optical properties, especially the solute-solvent interaction energy (stabilization energies) of the ground and excited electronic levels of the dissolved solute because of the differences in the dipole moments of the two states which are functions of the symmetry and multiplicity of the ground and excited state of the orbitals concerned (Denisio *et al.*, 2004).

Also, depending on the nature of the solvent, the vibrational fine structure which normally accompanies electronic transitions may be blurred, broadening or completely obliterated due to the varying degrees of the perturbation of the potential energy surface of the two states (Kalyamasunderam and Thomas, 1977). Substantial blurring has been correlated with hydroxylic solvent (Ucark-Astarlioglu, 2003). Kasha (1950), and Kasha *et al*., (1965) have shown that n→π* transitions are greatly blurred in solutions than π→π* transitions. Jaffe and Orchin (1962) also attested that, from well resolved electronic absorption or emission spectra, the vibronic structures of electronic transitions are the only experimental means of determining the excited state vibrational frequencies of molecules.

Many studies had been carried out on the effects of solvent on the absorption spectra of molecules using classical theory (Bayliss, 1950; Jun and Daiqian, 2004., Tetsuya *et al*., *2011*) or quantum mechanical perturbation theory (Thomas *et al*., 2008, Ya-Ying *et al*., 2008). Comparison of the absorption spectra properties of molecules in the vapour phase and in the solution by many researchers (Luzhkov and Warshel, 1991; Stavrev *et al*., 1995; Kyril *et al*., 1998) show that solvent effects may be classified into:

a. The dielectric effects, which from molecular point of view is termed dipolar interaction.

b. The dispersive interactions due to Van-der Waals forces which exist in all solute-solvent systems.

c. The short range specific interaction between the solvent and solute molecule i.e. electron transfer, hydrogen bonding effect and columbic charge transfer interactions.

d. The associative effect between the solute molecules, which affect the solute concentration and may be eliminated at low concentration of the solute.

e. The electrochemical effect i.e. the changes in the degree of disassociation of the solute in different solvent which is studied by varying the pH of the medium.

f. The long range intermolecular resonance effect that manifests itself in the type of substituent and its position on the rings of the solute molecules (substituent effects).

g. The polarization or inductive effect which manifests itself if the solute is non polar.

Solvent properties vis-à-vis the nature of solute-solvent interactions affects the position, shape and intensities of the electronic absorption bands.

On the basis of the shift in the position of absorption or emission bands upon the dielectric variation of the solvent, empirical classifications of electronic spectra has been established into either positive or negative solvatochromic depending on whether the shift is to higher or lower wavelength (Harry *et al*., 2000; Sujarat *et al*., 2000; Praveen and Ojha, 2012). This helps in the adequate knowledge and determination of various molecular structures, chemical reactivities and properties of the solute. These are the transition polarizabilities ($\Delta\alpha$) and transition dipole moments ($\Delta\mu$) in the case of solvent perturbation of the transition energy, transition moment, transition polarization and vapour phase oscillator strength (*f*) in the case of solvent perturbation of the oscillator intensities, excited state vibrational frequencies and potential energy surfaces in the case of the solvent effect on the shapes and fine structures. Other chemical concepts and reactivity indices such as frontier orbitals [Highest Occupied Molecular Orbitals (HOMO) and lowest Unoccupied Molecular Orbital (LUMO)] energies, electronegativity, chemical potential (χ), global chemical hardness (η) and electrophilicity index (ω) have also attracted considerable attention of recent. This detailed information helps in the understanding of the photophysics and photochemistry of molecules (Kawski, 2002; Ya-Ying *et al*., 2008; Abdul-Raheem *et al*., 2010; Udhayakala *et al*, 2011). Theoretical investigations into these properties are also of importance in the study of the relationship between structures, properties and performance; and in the development and synthesis of derivatives of new compounds with improved properties. However, few works have been reported in this area, especially in the comparative molecular calculations of photo-physical properties for better understanding of the molecular structures, along with using such information to predict the chemical stabilities and activities of compounds (Udhayakala *et al*., 2011).

Generally, the oscillator strength of an electronic transition which constitutes the absorption intensity may derive its strength through the intensity borrowing phenomena, primarily by mixing of the state of solute weak or forbidden transitions with that of a much allowed transition density of the solvent (Orlandi and Siebrand, 1972)˙ This is theoretically related to the square of the transition moment and experimentally to the integral molar absorptivity of dissolved solute according to Liptay's formalism (Liptay, 1969). This yields the expression in *1.1*

$$\int \varepsilon_{(v)} dv = kv|\mu_{ij}|^2_{osc} \qquad 1.1$$

$$\text{where } k = \frac{8\pi^3 N_0}{10^3 (ln\,10)^3 hc} \qquad 1.2$$

μ_{ij} is the transition moment between state *i* and *j*. N_o is the Avogadro's number, *h* the Planck's constant, *c* the speed of light and *v* is the average frequency of the absorption band. The square of the transition moment for a three dimensional harmonic oscillator, from ground state to the excited state is given as:

$$|\mu_{ij}|^2_{osc} = \frac{3he^2}{8\pi^2 m_e v} \qquad 1.3$$

The oscillator strength *f* of a transition with transition moment $|\mu_{ij}|$ is given by:

$$f = \frac{4m_e c\varepsilon_0}{N_0 e^2} \int \varepsilon_{(\bar{v})} d\bar{v} \qquad 1.4$$

where m_e, is the mass of the electron. For a single electron undergoing more than one transition; the sum of the oscillator strength for all the transitions arising from one level to all levels is unity i.e $\sum_i f_i = 1$.

Thus, the transition moment of the solute in the solution due to the modification of the effective field of the solute becomes:

$$|\mu_{ijs}| = |\mu_{ijv}| + \alpha_{ij} F_{RM} \quad 1.5$$

where $|\mu_{ijs}|$ and $|\mu_{ijv}|$ are the transition moments of solute in the solution and that of free molecules (vapour phase) respectively, α_{ij} denotes the transition polarizability, while F_{RM} is the reaction field and $\alpha_{ij} F_{RM}$ is the solvent parameter which directly influences spectra intensities of solutes determined in different solvent.

The solvent environment modifies the charge densities (i.e polarizabilities) of dissolved solutes. This appears in the form of intensity borrowing formulation and transition densities (Spry *et al*., 2006). Also, the effect of substitution in molecules does not produce great changes or new bands in the spectra, but modifies the spectrum of the parent compounds. And, like solvent, it affects the transition energies, the intensity of transition and the vibrational fine structure (Nicolae, 2002; Natasa *et al*., 2006; Abdul Raheem *et al*., 2010).

2.1 Applications of some of the compounds studied

The chemistry of hetero-aromatic, carbonyl compounds and their derivatives are important parts of organic chemistry for their theoretical application, variation in their synthetic procedure, as well as, their physiological significances (Suschitzky and Scriven, 1981; Gilchrist, 1992). The discovery of hetero-aromatic substances play important roles in the metabolism of all living cells and the ever increasing large scale production of these molecules and carbonyl compounds are finding important uses in the industries and researches as starting materials for the synthesis of larger, usually bioactive structures (Warshel and Lappicirella, 1981; Gribler and Gilchrist, 2002). Among these important substances are the antibiotic drugs like nitrofurantoin, vitamins and coenzymes precursors such as riboflavin and nicotinic acid (Warshel and Lappicirella, 1981).

1.1.1 Benzo[b]thiophene (BT) and 3,4-diphenylthiophene (DPT)

Benzo[b]thiophene (Figure 1.1) exhibits a broad spectrum of biological and pharmacological activities as selective oestrogen receptors and modulators for treatment or prophlaxis for prostate cancer, benign hyperplasis and nervous disorder (Blicke, 1952). They are found within the chemical structures of pharmaceutical drugs like zilenton, sertaconazole and raloxifene which are important antimicrobial, and as manufacturing agents for dyes like thioindigo, (Alberts and Leonards, 1973; Wang *et al*., 2009-11).

2,3-diphenylthiophene (DPT**)** and its linear organic π-conjugates derivatives are also useful when suitably modified, in the low cost fabrication processes of stable, large-area, and lightweight electronic devices like mobile phone and computer displays (Kinga *et al*., 2011).

1.1.2 9,10-Phenanthrenequinone (PQ) and it derivatives

Polycyclic aromatic hydrocarbons (PAH) have earned considerable attention because they are widely distributed in the environmental and are toxic. These toxic effects vary significantly between polycyclic aromatic hydrocarbons and it includes acute toxicity, carcinogenicity and teratogenicity (Lavoie *et al*., 1979). In the environment, PAH decompose by a variety of biotic and abiotic pathways. For example, many PAH show strong absorbance in the solar ultraviolet region and undergo rather favourably photolysis reactions in air, water or solid phases (Larson and Weber, 1994). They can also be degraded by bacteria and fungi (Carniglia, 1984).

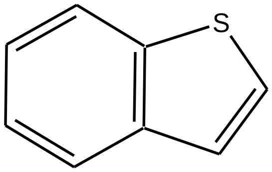
Phenanthrene, the parent compound for 9,10-phenanthrenequinone (Figure 1.1), is a three rings PAH commonly found in petroleum distillates and products derived from coal such as creosote. In either polar or non polar environments, it is converted by sunlight into a more polar PQ and subsequent oxidation products such as the corresponding ring-opened dicarboxylic acid products (Barbas *et al*., 1996). Photo oxidation generally increases the toxicity of PAH to eukaryotes (Arfsten *et al*., 1996) due to the production of toxic products such as quininones. PQ in particular has been described as being toxic to a greater extent than its parents compound in a bacterium (*Photobacterium phospherum*), found in plant duckweed (*Lemna gibba L.*) (Mc-Conkey *et al*., 1997). It also inhibits endogenous respiration in an activated sludge while the parent compound, phenanthrene would not.

Several studied of marine system, have shown increase biodegradation of PQ compared with the parental compounds (Duta and Harayama, 2000; Jonathan *et al*., 2005). This has also been shown in the soil and sewage sludge (Miller *et al*., 1988) and laboratory cultures (Nimatuzahroh *et al*., 1999; Lehto *et al*., 2000). Thus, the photochemistry and spectroscopic properties of this azo dye compound (PQ), which is an effective starting agent for the preparation of many antimicrobial agents; phenanzine and their derivatives (Adeoye *et al*., 2009) worth studying.

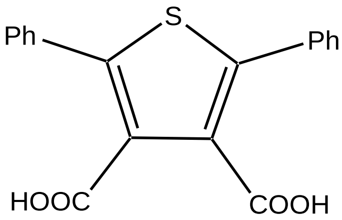
1.1.3 2,3-diphenylcyclopropenone (DPCP)

Carbonyl compounds are widely spread in nature; often combined with other functional groups. They are chiefly found in plants or microorganisms but some have animal origin. The carbonyl oxygen of DPCP is more basic than most ketones, as a consequence of comparatively high polarization of the carbonyl group (Hanton and Banwell, 1987).

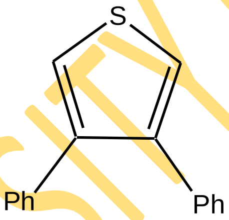
DPCP has a variety of applications, ranging from its use as starting material for various acid–base complexes (Robert *et al*.,1989) and as symptomatic and immunosuppressive therapy to diminish the manifestation of alopecia areate diseases (Galadari *et al*., 2003). Many researchers (Aghaei, 2005; Firooz *et al*., 2005) have also claimed its high efficacy as topical sensitizer in the treatment of alopecia areata. Treatment of alopecia with DPCP is based on criteria like age and the extent of the disease (Firooz *et al*., 2005). Although, it is non–mutagenic but highly sensitive to ultraviolet light degradation and so needs be kept from light to maintain its effectiveness.



Benzo[b]thiophene C_8H_6S (BT), MM = 134. 02 $gmol^{-1}$



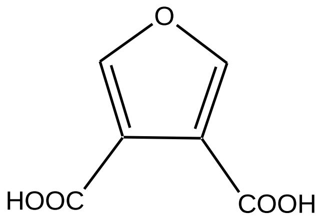
3,4-dicarboxylic-2,5-diphenylthiophene $C_{18}H_{12}SO_4$ (DCDPT), MM = 324.35 $gmol^{-1}$



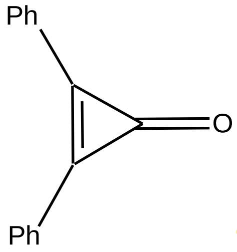
3, 4-diphenylthiophene $C_{16}H_{12}S$ (DPT), MM = 236.07 $gmol^{-1}$

MM: Molecular Mass

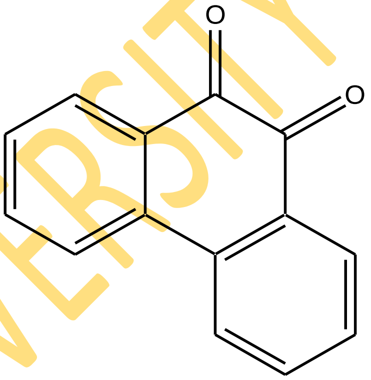
Fig. 1.1: Names and molecular structures of the compounds investigated



Furan-3,4-dicarboxylic acid $C_6H_4O_5$ (DCF), MM = 156. 09 $gmol^{-1}$



2,3-diphenylcyclopropenone $C_{15}H_{10}O$ (DPCP), MM =206.24 $gmol^{-1}$



9,10-phenanthrenequinone $C_{14}H_8O_2$ (PQ), MM = 208.21 $gmol^{-1}$

MM: Molecular Mass

Fig. 1.1 contd.: Names and molecular structures of the compounds investigate

1.2 Justification for the study

The various applications of heteroaromatic and carbonyl compounds and the remarkable fact that certain physical and chemical properties of thiophene, furan, benzene and their derivatives are similar makes us consider it worthwhile to study the spectral and photo-physical properties of some of the derivatives of these compounds. These are furan-3,4-dicarboxylic acid (FDC); 3,4-dicarboxylic-2,5-diphenylthiophene (DCPDT), 3,4-diphenylthiophene (DPT) and benzo[b]thiophene (BT) (Figure 1.1). Also, 2,3-diphenylcyclopropenone (DPCP), despite its highly strained ring is relatively stable compound, its photochemistry and spectroscopic properties worth studying.

Moreover, due to the fast progress in photochemistry, variety of approaches to the theoretical and experimental treatments of solvent and substituent effects have been developed and applied to the studies of organic reactions and dynamic processes in solution, as well as, to studies of ultraviolet-visible spectroscopic phenomena to determine the transition polarizability ($\Delta\alpha$) and transition dipole moment ($\Delta\mu$) of molecules. These include: the solvent frequency shift of electronic spectra method (solvatochromism) (Abe and Iweibo, 1985a; Mariola and Naggy, 1988; Kyril, 1998), electro-optical methods of absorption and the effect of external electric field on the fluorescence anisotropy (i.e Labhart- Liptay molecular electrochroism) (Kawski, 2002; Tayama *et al.*,2009) and theoretical treatment using, configuration interaction treatment (Schrimer and Trofimov, 2004), in which the computation of excited state properties and moment is straight forward, Time-Dependent Density Functional Theory (TD-DFT) (Cassida, 1994; Gronzenman *et al.*, 2001), stark splitting of rotational levels of the *0–0* vibrational band (Baumann *et al.*, 1989), and other molecular orbital calculation methods (Pople and Beveridge, 1970; Hebert *et al.*, 2006).

However, none of these methods has gained general acceptance and applicability, as most of them either suffer various difficulties in the operation of their theories or experiment or their applicability to larger molecules. The restriction due to the inherent size inconsistent error in the use of Abe's theory (Equation 2.13) of solvatochromism, which is more pronounced for properties other than excitation energy make the results of the determination of these photophysical properties of molecules by different models to show large spread (Warshel and Lappicirella, 1981; Helgerker *et al.*, 2000; Schirmer and Trifimov, 2004). The laborious and expensive nature of electro-optical experiment restricted their use to few laboratories while the molecular orbital calculation method is being continually refined and tested for internal consistency since its theories are often made under the assumptions that may be limited in validity or scope. These setbacks pave the ways to the development of cheaper and more acceptable models for determining these parameters by different researchers.

In this investigation, a quantum-mechanical perturbation theory that accommodates intensity parameters such as solvent molecular polarizability (α), the molar refraction (R), stark term (μ/r^3) and Einstein coefficient (k_{ji}) and oscillator intensity (f), using the scope of Iweibo *et al.*, (1991) and adopting partly, the Louguett–Higgins and Salem (1961) mode of intermolecular forces, which is effective in revealing the factors governing intensity enhancement was employed. These were used in developing a linear regression model which was then applied in determining the $\Delta\alpha$ and $\Delta\mu$ of FDC; DPT; DPCP; BT; DPCP and PQ (figure 1.1) with the principle of absorption spectrophotometry in order to study their activities and reactivities. The observed values of these photo-physical parameters are then compared with those obtained by molecular orbital calculation by means of Time-Dependent Density Functional Theory, using B3LYP function with 6-31G* basis set (TD-DFT B3LYP/6-31G*). This has been proved to produce qualitatively acceptable and accurate spectra along with calculations of molecular vertical excitation energies, transition polarizabilities, and transition dipole moment for the modeling of spectroscopic probes. It has also been claimed to adequately address the structure –function relations for predicting structures with desirable optical properties (Tretiak *et al*., 2000).

Moreover, this research was also conducted in order to elucidate the nature of inter molecular interactions leading to the charge transfer between the Electron Donor-Acceptor (EDA) moieties in these compounds. The characterization of the response of the bands of these molecules to specific solvent properties (medium impact) is expected to enhance their use as spectroscopic probes for complex systems and this type of study has potential uses for industrial applications as some heteroaromatic EDA systems showing the dual Absorption/fluorescence can be used in the fabrication of molecular switches and photovoltaic cells (William *et al*., 1999).

The choice of these compounds is based on their various applications, the variation in their structures (Figure 1.1) and on the need to justify the theoretical expression for the adapted solvatochromic shift method, and in parts, to determine the accuracy and the internal consistency of the results obtained from the methods used or to reveal any discrepancy in both methods of measurement.

1.3 Research objectives

The vibrational fine structures which usually accompany the electronic transitions may be blurred, broadened or completely obliterated due to varying degrees of perturbations of the Potential Energy Surfaces (PES) of the ground and the excited states of the solute molecules which manifest itself in the observed differences in the electronic polarizability ($\Delta\alpha$) and dipole moment ($\Delta\mu$) of the excited state relative to ground state of the molecules. These two parameters are the most sought after spectral parameters of the excited molecules and their knowledge often aids in revealing the excited state configuration or structures of molecules and their reactivities (Ayachit *et al*., 1986; Kawski, 2002; Ya-Ying *et al*., 2008).

Moreover, the configurations of most compounds and their corresponding derivatives are governed by ranges of factors, such as:

a. The type, number and position of the substituents whose effects can be mesomeric (delocalization), inductive and /or steric.

b. Solvent preferential stabilization of a particular configuration or set of configurations.

c. Charge transfer and structural change through the process of absorption of photon.

Thus, the specific objectives of this research work are to:

i. Study these factors quantitatively to determine the extent to which they have contributed in determining the assumed molecular configuration of the studied compounds by means of the solvent and substituents perturbation of the band shapes, transition intensities and frequencies of the electronic spectra of these molecules.

ii. Determine the experimental oscillator strength values for the compounds under investigation both in the vapour and solution phase, using the scope of modified Onsager-Abe model (Iweibo *et al*., 1990).

iii. Correlate the properties of these solvated solutes of interest to that of the vapour and in part identifies the important terms that contribute to oscillator parameter in solution based on the modified Onsager-Abe model (Iweibo *et al*., 1990). The combined effects of solvents and substituents on the transition energies of the compounds will also be investigated.

iv. Determine the spectral parameters of the excited molecules, i.e, the transition polarizability, Δα and transition dipole moment, Δμ, using the modified solvatochromism frequency shift equation which incorporate the intensity parameters through the partial adoption of Louguett–Higgins and Salem (1961) mode of intermolecular forces into the scope of Iweibo *et al*., (1991).

v. To carry out quantum chemical calculation on the studied compound using a computer oriented Time Dependent Density Functional Theory (TD-DFT B3LYP/6-31G*) calculation which has been found to be an exact theory or local density approximation to describe the dynamic response of many particles systems to external perturbations in order to give accurate results for polarization (α), dipole moment (μ), Excitation Energy (EE), HOMO-LUMO energy gap ($E_{LUMO\,-\,HOMO}$) and other quantitative structure-activity/properties relationship (i.e QSAR/ QSPR).

vi. Make quantitative and qualitative comparison of the results obtained from these two models (i.e modified solvatochromic shift scope of Iweibo *et al*., (1991) and the Louguett – Higgins and Salem (1961); and the theoretical /computational techniques).

CHAPTER TWO

2.0 LITERATURE REVIEW

The absorption of organic compounds is determined by two factors; the skeleton of the unsaturated bonds and the radicals or groups attached to the skeleton (Crammer and Truhlar, 1994). Therefore, the perturbation of electronic spectra transition intensities, frequencies of molecules and correlation of these changes with molecular properties and structures of ground and excited state of compounds are better understood when their photophysical properties are treated empirically, theoretically and by the use of computational technique.

2.1 Empirical treatment of photophysical properties of the compounds

Spectroscopic properties of some compounds have shown pronounced changes in the spectra intensities of dissolved molecules compared with molecules in the free state and when these molecules are transferred from one solvent to another. These variations were accounted for by most spectra intensity theories (Rector *et al.*, 1998) by considering different factors contributing to these changes. Factors such as local field at the solute site which the environment introduces, the changes in solute charge densities of the molecules or electron distribution (i.e. polarizability) and the effect of refraction by solvent have been considered by different researchers (Walter *et al*., 1999; William *et al*., 1999). The perceptions of these effects and the problems encountered in the conversion of spectroscopic parameters measured in solution to those measured in the vapor and vice versa have helped to stimulate theoretical developments which describe more accurately these phenomena.

2.1.1 Solvents modification of electronic absorption intensities

Shuyer (1953) submitted that the earliest study on the correlation of the spectral intensity changes in the nature of solvent was by Chacko in 1934. He used Lorentz local electric field of a photon in solution and classical dispersion theory to assess the effect of non-polar solvent on an electronic transition in deriving the expression relating the molar extinction coefficient of a dissolved substance, the refractive index *(n)* for the solvent and the imaginary part of polarizability which is taken to be the same as that of free molecules. He related the molar extinction coefficient of a dissolved substance with the refractive index of the solution (Equation 2.1) and also correlated the apparent oscillator strength in solution to that of solute in vapour phase as presented in equation *2.2*.

$$\frac{n\,k_m}{n^2+2} = \text{constant} \qquad 2.1$$

where k_m is from the well known absorption law of Lambert-Beer i.e. $I = I_0\, e^{-k_m cx}$

I_o is the initial intensity of light, I the intensity light after traveling through a distance x(cm) through the solution i and C, the concentration of the absorbing substance in mol/litre.

$$\frac{f_{sol}}{f_{vap}} = \frac{(n^2+2)^2}{9n} \qquad 2.2$$

This expression concluded that the correction factor for the oscillator strength on changing from vapour phase to dilute solution is $\frac{(n^2+2)^2}{9n}$. Equation *2.2* is applicable to only allowed transitions in non-polar solvents, as the local filed does not consider the translational fluctuations in polar fluid (Linder and Abdul-nur, 1971). It also excludes solvent environment on the charge density of the solute.

Kirkwood (1936; 1939) generalized the Onsager's theory and derived the expression for the intensity of a microscopic spherical specimen of dielectric produced by a fixed molecule in its interior. Similar treatment was also presented by Clifford and Crawford

(1966). Shuyer (1953) formulated the solution–solute vapour intensity ratio, $\frac{f_{sol}}{f_{vap}}$ using Onsager-Bottcher reaction field and classical theory. He also related $\frac{f_{sol}}{f_{vap}}$ to solvent refractive index *(n)*, solute polarizability *(α)* with effective cavity radius (*r)* as in equation *2.3*.

$$\frac{f_{sol}}{f_{vap}} = \frac{3n^2(n^2-1)}{(n^2+2)(2n^2+1)(1-\alpha f_{(n)})} \qquad 2.3$$

where the Onsager reaction field function $f_{(n)}$ was defined as: $f_{(n)} = \frac{2(n^2+2)^2}{r^3(2n^3+1)}$.

This expression, to a certain extent accounts for structural fluctuations in all fluids. Bakhshiev and co-workers (1963), while analyzing various factors contributing to spectra intensity changes derived an expression for the changes in terms of effective Einstein coefficient “k_{jis}” and retained classical theoretical approach to the description of solution – solute vapour intensity ratio $\frac{f_{sol}}{f_{vap}}$. Ab initio calculations of the polarizability effect were attempted by Weingnang (1964), Liptay (1966) and Robinson (1967). Using second order perturbation theory, these investigators determined the $\Delta\mu$ of the solute resulting from the action of the neighbouring molecules. Robinson’s treatment was formulated for a single perturber at a fixed inter-nuclear distance from the solute, and by applying second order perturbation theory; he identified mechanisms by which weak transitions of solute molecules could borrow intensity from other allowed solute transitions and transition of solvent molecules.

Weignang (1964) considered many perturbers concentrically located about the dissolved molecules. Using the Onsager reaction field, Weignang (1964) and Liptay (1966) came up with the expression relating the integral absorptivity to the dipole moment in terms of some solvent correction factors as defined in equation *2.4*

$$\frac{3\hbar c}{4\pi^{2}N}\int \varepsilon_{(\bar{v})}\,{}^{\partial\bar{v}}/_{\bar{v}} = \left\{\frac{n^{2}+2}{9n}\right\} f(n,\varepsilon)\mu_{iv} \qquad 2.4$$

where the term in the { } bracket is the Lorentz field correction factor of Chako (1934), $\mu_{i,v}$ is the electric dipole strength in the vapour state, $\mathcal{E}_{(v)}$ is the molar absorptivity at frequency (v) and

$$f(n,\varepsilon) = 1 + Af_{(n_{ji})} + Bf_{(n)} - C\left[f_{(s)} - f_{(n)}\right]^{2} D_{i(s)}$$

$f_{(n)}$ is the Onsager reaction field function at zero frequency previously defined in equation *2.3*, $f_{(n_{ji})}$ and $f_{(s)}$ are the corresponding terms of the transition frequency and for the dielectric constant ε functions respectively. $D_{i(s)}$ is the square modulation of the transition moment in the vapour phase. The terms *A*, *B*, and *C* represent the perturbations of the molecular density by dispersion, dipole-induced dipole and the interacting permanent dipole moment of the solute and solvent respectively, all of which constitute the Van-der Waals interaction and correct for the effect of solvent on the solute electron density.

However, Robinson (1967) and Weignang (1964) treatments have their limitations; while Weignang model is too rigid to be applied to fluid, Robinson treatment does not account for the quantum statistical aspects of the problem. Linder and Abdul-nur (1971), Abdul-nur (1973), Myers and Birge (1980) and Shibuya (1983) have also used perturbation theories. Linder and Abdul-nur's theory used quantum statistical double perturbation theory to derive a virial expression of the oscillator strength in a non-polar medium and correlated the virial coefficient with various combinations of transition matrix element in a manner similar to that of Weignang. Myer and Birge (1980), in their critical examination of the effect of solvent on the transition moment of cylindrical model introduced by Christen and Straub (1973) on the description of the oscillator intensity in solution, proposed a general theory on the effect of the geometrical shape of solute and the orientation of transition moment relative to solute molecular axis. They limited their consideration to the dispersion interaction and expressed the perturbative correction factor of the transition moment to a function of refractive index by neglecting the field correction of the light waves. This theory predicted a decrease in the oscillator strength of π-π* transition of β-carotene and an increase in the oscillator strength of n-π* transition in pyrazine. But classical field theories (Jacobs and Platt, 1948) predicted that the oscillator strength should change in the same direction.

Bayliss and Wills-Johnson (1968) used the modified version of the reaction field employed by Linder and Hoernschemeyer (1967) in the treatment of Van-der Waal forces. Koyanagi (1968) deduced the field from London dispersion formula. The methods used by these workers replaced the effect of the surroundings by a field in the techniques that take into consideration the local field and polarizability effect. This is termed "field simulation method". Abe (1970), in his application of the Onsager model and quantum mechanical perturbation theory, derived the theoretical expression in *2.5* for an electronic transition of a molecule embedded in an isotropic continuous medium of solvent.

$$\frac{f_{sol}^{theor}}{f_{vap}^{theor}} = \frac{9n^2}{(2n^2+1)^2}\left(\frac{\bar{v}_{sol}}{\bar{v}_{vap}}\right) \qquad 2.5$$

where $\bar{v}_{sol}$ and $\bar{v}_{vap}$ are the transition wave numbers in solution and in vapour phase respectively. The ratio of the wave number in solution and vapour phase, as additional multiplicative factors to that of Bakshiev corrects to some extent for solvent effect on the electron density of solute.

Chongwain (1994) reported that the use of Onsager field by Abe (1970) which predicted a decrease in $\frac{f_{sol}}{f_{vap}}$ as opposed to that described by Lorentz field reopened the controversy on the prediction of the direction of the magnitude of $\frac{f_{sol}}{f_{vap}}$. This controversy eventually led to the earlier suggestion of Milliken and Rieke (1941) which stated that the refractive index correction factors should be set to unity. He further stressed that the $\frac{v_{sol}}{v_{vap}}$ ratio may not be important for small perturbations of electronic energies which arises from inconsistency in the definition of the oscillator strength in solution.

Abe and Iweibo (1985b) affirmed that the non uniformity in the refractive index correction term in the expression for the Oscillator strength was due to alternative fundamental definitions of the intensity terms. They later derived equations *2.6* and *2.7* as experimental and theoretical expressions for the oscillator strength of a solution of an assemblage of molecules where μ_{oisol} is the transition moment of the molecules in solution, ν_{oi} the wave number of o → ί transition, $\mathcal{E}_{(\mathrm{v})}$ the molar absorptivity coefficient at wavenumber $\bar{v}$, c the speed of light in vacuum, h the Planck's constant , e the charge of photon, m_e the mass of an electron while $\mathrm{N_o}$ is the Avogadro's constant.

$$f_{sol}^{expt} = \frac{4n(10^3 ln 10 m_e\, c^2)}{(1+n)^2(\pi e^2 N_0)} \int \varepsilon_{(\bar{v})} \partial\, \bar{v} \qquad 2.6$$

$$f_{sol}^{theor} = \frac{3n^4(8\pi^2 m_e c\bar{v}_{0i})}{(1+n)^2(2n^2+1)^2(3he^2)} |\mu_{0isol}|^2 \qquad 2.7$$

The definition of Abe and Iweibo (1985b) for the oscillator strength removed ambiguities in the expression for oscillator strength from solvent to solvent as it allows for comparison of oscillator data from solvent to solvent. A much more improved equation was later developed by Iweibo *et al.*, in 1990. This involved both field and quantum mechanical correction to the transition moment. And in this work, Einstein coefficient (k_{ijs}) was asserted to embody solvent microscopic properties. The new definition of k_{ijs} and the radiation density permits field correction factors to be introduced without much ambiguity in the experimental expression for the oscillator strength. Also, Iweibo *et al.*, (1990) corrected the Lambert's law by introducing the solvent correction factor mainly due to the effect of instrumental optics on the measurement of absorbance. With these modifications, these researchers proposed equations *2.8* and *2.9* as the description of the experimental and theoretical oscillator strengths respectively.

$$f_{sol}^{expt} = \frac{Vmb}{N_0 \pi e^2}(ln10)\frac{cv_{jis}}{\hbar}\int \varepsilon_{(\bar{v})}\frac{\partial\bar{\upsilon}}{\bar{\upsilon}} \qquad 2.8$$

$$f_{jispo}^{theor} = \frac{8\pi^2 v_{jiv}}{3e^2}\left|\mu_{jis}\right|^2 \frac{\Pi \,{}^{\beta_{is}}\!/_{\beta_{1s}}}{\Pi \,{}^{\beta_{iv}}\!/_{\beta_{1v}}} \qquad 2.9$$

In these equations, *m* and *e* are mass and charge of electrons respectively, *n* is the refractive index, *c* the speed of light, $\varepsilon_{(v)}$ being the molar absorptivity at frequency v_{jis} , as defined by Bouguert-Lambert–Beer law, N_o is the Avogadro's number, *V* the volume of solution, *h* is the Planck's constant, while μ_{jis} is the solute transition moment from state ί to state j in solution, $b = 4\pi\varepsilon_o$ in the S.I unit and unity in c.g.s unit, ε_o is the vacuum permittivity, β_{is} is the square modulus of a solvent correction factor. This improved method, unlike previous ones on field models which assumed the cavity occupied by the solute to be empty, proposed a model in which the cavity is not empty but is filled with materials of the solute and or solvent. It also accommodate systems in which the solute potential energy surfaces in the solution differ substantially from those of the vapour owing to large alterations on the vapour phase molecular dimension and internal field functions by solvent (Lesi, 1996). The improved equation of Iweibo *et al*., (1990) constitutes the basis for determining the oscillator strength and other electronic transition parameters in this study.

2.1.2 Solvent modification of electronic spectra frequencies

The dependence of electronic spectra of solute molecules on the dielectric properties of solvents media has been used to establish the empirical classification of electronic spectra (Murrel, 1963; Ooshika, 1954), as the experimental data on the effect of solvents on the position of bands in two spectra can give valid information on the type of transitions and molecular basis of the shift responsible for the bands (Kemp, 1991). The difference in the frequency of electronic transition of molecule in solution and in the vapour phase may or may not be profound, and in some cases, the general shape of the spectrum is unaltered.

The shift in the frequencies of electronic absorption transitions has been the subject of many investigations with the focus on defining the molecular basis of the shift. In solution however, because of various molecular interactions, the vibrational bands are usually broadened and partially reduced in number while the rotational lines become obliterated or unobserved. The solute-solvent interactions may be non specific (weak Van-der Waal forces), specific interaction if the solvent modification of absorption frequency is small or specific interaction whose effect superimposed on the universal weak Van-der Waal forces for the interaction of solvent and solute that leads to electron exchange between the solute and the solvent. This causes pronounced changes in the spectra features of solute. Examples of which include hydrogen bonding, charge transfer between the solute and the solvent, complexation, isomerization and ionization interaction (Chongwain, 1994). According to Nicol (1974), the energies of non-specific interaction are generally attributed to:

i. The interaction between permanent dipoles of the solute and solvent.

ii. The interaction of the permanent dipole moment of the solute with the induced dipole of the solvent by the solute dipole.

iii. The interaction of the mutually induced dipoles (polarizations of electron clouds) of the solute and solvent (i.e dispersion effect or London forces) London, 1937.

iv. The interaction of the permanent dipole moment of the solvent with the dipole moment induced in the solute by the solvent (Linder, 1960).

Thus, the problem of solvent effect is considered as physical perturbation of the relevant molecular states of the solute (Bakheshiev, 1961; Liptay, 1969). The expressions from the perturbation theory are then connected with the macroscopic properties of the solvent and the solute by means of various models; such as, Lorentz and Onsager fields and some modifications of the Onsager field. In all the theories of solvent frequency shift, the solute molecules are considered as dipoles which undergo the influence of the internal field of the solvent. The difference between the magnitudes of this dipole in the ground and excited states of the molecules determined the extent of the change in the relative position of the energy levels and the extent of the frequency shift (Evale *et al*., 2009).

Bayliss (1950), Bayliss and Mc-Rae (1954) in their pioneer works on the correlation of solvent spectra shifts of solute electronic spectra with the field of the bulk solvent attributed the bathochromic shift observed in the spectra of the non-polar solutes in non-polar solvents to the solvation energies of the Δμ of the solvent in both the ground and excited state owing to polarization effect and dielectric constant of the solvent. And, they quantitatively predicted that the frequency shift (Δv) is given by:

$$\Delta v(cm^{-1}) = \left[\frac{3e^2}{8\pi^2 c^2 m}\right]\frac{f_{ij}\left(n^2 - 1\right)}{Va^3\left(2n^2 + 1\right)} \qquad 2.10$$

e is electronic charge, c is the velocity of light in vacuum, m the mass of electron, f_{ij} the oscillator strength of the transition in the solute, a the radius of a spherical cavity of volume, V (cm^3). Bayliss expression treated the solute perturbation in term of the dispersion since the refractive index term is the Onsager reaction field expression for the polarizability of the solvent and *f* relates to transition polarizability of the solute.

By employing second order perturbation theory, Mc-Rae (1957) proposed that the frequency shift in solution Δv arising from interactions involving solute permanent dipoles, superposed on the polarization red shift is given by:

$$\Delta v = \left[AL_0 + B'\right]\frac{n_D^2 - 1}{2n_N^2 + 1} + C\left[\frac{D-1}{D+2} - \frac{n_D^2 - 1}{n_D^2 + 1}\right] + E\left[\frac{D-1}{D+2} - \frac{n_D^2 - 1}{n_D^2 + 2}\right]^2 \qquad 2.11$$

where *A*, *B*', C and *E* are constant characteristic of solute, Δv is the difference in the solute absorption frequency in the solution relative to the vapour phase while D and n are the dielectric constant and the refractive index of the solvent respectively. This equation has also been used to explain the frequency shifts in different solvent systems by neglecting the stark term and the dispersion term which effectively reduces the number of variables in the Mc Rae's equation. It has also been utilized in studying the effect of dielectric permittivity term by measuring the frequency shifts in polar solvents of nearly the same refractive index but of different dielectric permittivity.

Ooshika (1954), Mc-Rae (1957), Weignang and Wild (1962), Natasa *et al.*, (2006) have also discussed frequency shifts in the spectra of polar solutes in terms of the relative solvation energies of the permanent dipoles, appropriated it to the contribution from either the combining states of the solute or to the resonance structures of these states. Ooshika (1954) and Natasa *et al.*, (2006) correlated the red-shift observed for the non polar solute in non polar solvent to dispersion interaction while Weignang and Wild (1962) treatment examined the relationship between frequency shift and bond densities of non-polar solvents. They correlated the relative shifts to dipole moment and polarizabilities of the bonds with tetracene as a model. Mc-Rae and Bayliss (1957) assertion of the red shift interpretation as given by equation *2.10* is inadequate if the solute is polar or other interaction forces such as hydrogen bonding and molecular complexation prevails Weignang and Wild (1962). Nicol *et al.*, (1968) also deduced an expression similar to Mc-Rae (1957) except that the modification reduces the terms in the equation to three as stated in equation *2.12*. This regarded solvent shift to compose of London forces and solvent Stark effect.

$$\Delta v = [A + C]\frac{n_D^2 - 1}{2n_D^2 - 1} + B\left[\frac{D - n^2}{D(n+2)^2}\right] + E\left[\frac{D-1}{D+2} - \frac{n_D^2 - 1}{n_D^2 + 1}\right] \qquad 2.12$$

where the constant *A*, *B*, *C* and *E* are as defined:

$$A = \frac{-1}{a^3}\sum\nolimits_{i=j} A_{ji}\left(\mu_{solute}^{ji}\right)^2 - \sum\nolimits_{j\mp 0} A_{0j}\left(\mu_{solute}^{0i}\right)^2$$

$$B = \frac{-108\ln^2\left(R/a\right)kT(\alpha_1 - \alpha_0)}{R^3}$$

$$C = \frac{-\left[\left(\mu_{solute}^{i}\right)^2 - \left(\mu_{solute}^{0}\right)^2\right]}{a^3}$$

$$E = \frac{-2}{3}\left[\frac{\mu_{solute}^{0}}{\mu_{solute}^{i}} - \left(\mu_{solute}^{0}\right)^2\right]$$

$$A_{ji} = 1 - {}^{v_{ji}}\!\!/_{v_{ij}}$$

μ^o and μ^i are the magnitudes of the parent and induced dipole moment of the solute respectively. The superscript represents the state of the solute and the symbol k is the Boltzmann's constant. R is the thickness of the solvent shell, T the absolute temperature while v is the transition frequency of the solute. D, a, Δv and α have been defined in the previous equations. Equation *2.12* shows that the refractive index of the solvent alone cannot account for the shifts in the frequency of absorption of molecules in polar solvents. Nicol, (1968) also observed that the blue or red shift on electronic frequency of absorption or emission depends on whether or not the dispersion effects are respectively less or more than the effects due to solute and solvent permanent dipole moment. Blue shift was predicted for polar solutes in polar solvents provided the transition dipole moment decreased during the transition while a red shift was predicted if the transition dipole moment increased.

Suppan (1990), in his own approach predicted a red shift for polar solutes in non polar solvents if the solute dipole moment increases during the transition. He concluded that for solvent of equal refractive indices, a subtraction of their solvent shift should eliminate the dispersion effects and hence permits obtaining the polarizability value of solute. This method has its own shortcoming but seems to be useful if only to give an order of magnitude of reliability. Excited state dipole moments (μ*) are however much easily estimated from the dipole–dipole term in this method, as well as in Mc-Rae's (1957) formulation if other contributing factors are negligible.

Different approximations of the Mc-Rae's equation have been used by various authors to correlate the spectral frequency shift with molecular properties. A plot of frequency shifts with various field functions of Mc-Rae equation give linear graphical representations from which either the μ^* or the excited state polarizability α^* may be determined. Amos and Burrows (1973) affirmed that the application of the dispersion term in determining α^* results in values subject to considerable uncertainty, as difficulties of accuracy occur in determining the dispersion term itself. Other approaches, especially those formulated on the reaction field model (Liptay, 1969; 1974) presumed that α^* is a little different from the ground state polarizability (α). But the results of the method of Abe (1965) yielded a large values of the excited polarizability when compare with that of ground state in most cases. Many other authors have also used equation *2.11* in its complete form (Weignang 1960 and Baur and Nicol, 1966). This equation in its various approximations yielded large changes in the dipole moment of the molecules in the ground and excited state and too large spread were reported for values of these changes. Prabhumirashi and Kunte (1986) suggested that the approximate forms of Mc-Rae (1957) expression might be sufficient in determining the excited state dipole moments and polarizabilities of molecules. This observation led to the reappraisal and the recasting of Abe's solvato-chromic model by Iweibo *et al*., (1991). And, the expression in *2.13* was obtained.

$$hv_{(s)} = hv_{(v)} - \left\{ \frac{2}{3} \frac{\left(\mu^{*2}_{a} - \mu_a^2\right)}{dkT} + \left(\alpha_a{}^{*} - \alpha_a\right) \right\} \sum_{i=1}^{N} \frac{\mu_{bi}^2}{dr_{abi}^6} - \frac{\left(\mu^{*2}_{a} - \mu_a^2\right)}{d}$$

$$+ \frac{3}{2} \left[\frac{\alpha_g^* I_g}{1 + \frac{I_g}{I_g^*}} - \frac{\alpha_g I_g}{1 + \frac{I_g}{I_e^*}} \right] \sum_{i=1}^{N} \frac{\alpha_g}{r_{abi}^6} \qquad 2.13$$

where v is the transition frequency, μ_g, α_g and I_g are the electric dipole moment, polarizability and the ionization potential of the solute or solvent ground electronic state respectively while μ_e^*, α_e^* and I_e^* are the corresponding excited state equivalents. The subscripts *a* and *b* represent the solute and solvent molecule respectively while the s and g are the solution and vapour phase respectively. The terms *"d"* is equal to $4\pi \in_0$ in the S.I unit (where ϵ_0 is the permittivity of free space which is a unity in c.g.s unit), while K and T are the Boltzman constant and temperature of the solution respectively, r is the van der Waals intermolecular distance between the centres of the solute and solvent molecules and the summation is extended over N solvent molecules interacting with the solute. The modification of this equation (Equation *2.13*) is one of the objectives of this research.

Martin *et al*., (2004), used averaged solvent electrostatic potential/molecular dynamic method to study theoretically the *n*→*π** electron transition in acrolein. The model combines a multi-reference pertubational treatment in the description of solute molecule with molecular dynamic calculation in the description of the solvent in order to demonstrate the importance of electron polarization and bulk solvent effect. Weizhong, (2004) theoretically studied the solvent effects on tautomerism and absorption spectra of 3-hydroxy-2-mercaptopyridine (HMP) and 2,3-dihydroxypyridine (DHP) *in vacuo* and in ethanol solution using the Density Functional Theory (DFT) at B3LYP/6-31G(d) level. The results indicated that the thione form of HMP and the keto form of DHP are the most stable tautomers in the equilibrium, and the energy barrier for the thiol-thione and enol-keto proton transfer decreases significantly when the tautomerism is mediated by a specific ethanol molecule in solution. The Time-Dependent Density Functional Theory - Polarizable Continuum Model (TD-DFT-PCM) calculations on all tautomers of HMP and DHP in vacuo and in ethanol have assigned the lowest *n*→*π** excitations of thione and keto tautomers to the observed absorption bands of HMP and DHP in solutions. The solvation is predicted to have relatively small effect on these *n*→*π** excitations in ethanol. Bakhshiev (2006) used an improved theoretical expression that describes the laws that determines how universal intermolecular interactions affect the matrix elements of the transition dipole moment in polyatomic molecules. When applied to the study of intense vibronic absorption bands of solution of non polar anthracene and a polar dye in various solvents, the result showed that the theory as a whole correctly described the experimentally observed dependence in both former and latter cases.

So far, it could be seen that the expressions for the solvent frequency shift varies according to different approximations made of the interaction energy between the solute and the solvent. Most works are approximations of Mc Rae's expression which is complex and not easy to evaluate. Thus, from the analysis of the various equations for frequency shift, the transition energy depends on:

a. Refractive index of the solute
b. The dielectric permittivity only when the static dipole moment of the molecule is changed by excitation.

The specific effect of the solvent on the spectrum of the solute also depends on the properties of the solute. Difficulties arise in the interpretation of the solvent effects as there are often slight changes in the second order perturbation type and can not be precisely measured. Also, the resultants of several individual effect which sometimes cancel out creates problem, as the most easily measured or often recorded solvent effect is the shift of the absorption maximum, but theoretical consideration of electronic energy state should be related to the position of the 0–0 band which is not necessarily affected in the same way.

2.1.3 Obscuring of the vibrational structures by solvent

The appearance of several absorption peaks or shoulders for a given chromophore is common to highly conjugated system; this is often associated with solvent environment. These fine structures reflect not only the different information on the molecular conformations that such system may assumed, but also the electronic transitions between the different vibrational energy level possible for each electronic states (Heostrasser 1968). The vibrational fine structures of this kind is mostly pronounced in vapour phase spectra and the existence of the vibrational bands in a transition could also reveal a displacement of the equilibrium nuclear position of the excited state relative to the ground state and or a change in symmetry during transition. Earlier studies (Obi-Egbedi *et al*., 1998; Benali, 2007) have reported blurring or obliteration of the vibrational fine structures in the absorption or fluorescence spectra on going from non-polar to polar solvent. The loss in the vibrational structure has been interpreted as due to specific solute-solvent interactions and the change in molecular geometry of the solute while the change in the Franck-Condon envelop accompany it is believed to be due to solvent modifications of the molecular potential energy surface (Sadhan, 1963; Reichardt, 2003). The Franck-Condon excited state is very transient owing to the relaxation of the solvent during a time of the order of the molecular vibrations. In terms of the principle of indeterminacy, this will prevent the establishment of the vibrational quantization in the excited state with the result that the vibrational structures of the spectrum are blurred· Also, a weak transition may borrow intensity from those of symmetry allowed vibrations (Strokash and Shigorin, 1978).

The photophysical studies of the absorption spectra of benzene in perfluorohexane by Hirayama (Kano and Yanagimoto, 1986) and by Choi and Lipsky (1981) suggested that saturated fluorocarbon solvent show minimal specific solvent–solute interaction in solution phase at room temperature. While Nakajima (1971, 1982) in his studies on solvent perturbation of vibronic bonds by pyrene in different solvents correlated the intensity enhancements of 0–0 band in the absorption and fluorescence of pyrene in various models vis:

(i) the solvent dielectric constant $\in$

(ii) Grinwald's parameter $\left[\dfrac{\in -1}{2\in +1}\right]$

(iii) the square of the relative quantity relating to dispersion energy $(\alpha_s/r^6)^2$ where α_s is the mean polarizability of the solvent and r the mean inter nuclear distance between the solute and the solvent

(iv) a factor taking into account the dispersion, ionization potentials of the solute (I_p) and the solvent (I_s) and an induction term arising from interaction between the solvent permanent dipole and the solute induced dipole:

$$f = \left[\frac{3/2\left(\dfrac{I_p I_s}{I_p + I_s}\alpha_s + \mu'\right)}{\gamma^{-2}}\right]^2$$

where μ' is the mean square of the solvent dipole moment.

(v) a factor that takes into account the polarizability of the solvent dielectric by the permanent dipole moment μ of the solvent: $f' = \left[\dfrac{\in +1}{2\in +1} - \chi\dfrac{n^2+1}{2n^2+1}\right]$

where χ is a variable parameter and n the refractive index of the solvent. He concluded that the contribution of various vibronic band intensities is from specific solute-solvent dipole-dipole coupling, although other effects due to π-orbital interaction between solute and solvent and bulk dielectric constant of solvent can not be neglected. Kalyanesunderam and Thomes (1977) in their studies of environmental effects on vibronic spectra of compounds and application to Miceller systems supported Nakajima *et al*., (1982) claims. He concluded that the contribution to vibronic band intensities is from specific dipole-dipole and dipole-dipole coupling, although other effects due to the π orbital interactions between the solutes and solvent, and the bulk dielectric constant can not be neglected.

Moreover, from the work of Harry *et al*., (2000) on peridinin and its derivatives, it was observed that spheroidenone solvent–induced broadening of absorption spectra occur only when substituent–induced broadening is present. This study attested to the influence of substituents also on the blurring or broadening of vibronic spectra of molecules.

2.1.4 Substituents modification of intensities, frequencies and band profile

It is known empirically that the absorption of an organic compound is determined by two factors (Finar, 1973; West, 1978):

a. The skeleton of unsaturated bonds, which is associated with the groups (chromophores) present.
b. The groups or radicals (auxochromes) attached to the skeleton or in conjugation with the electron of the chromophores. These are of two types:
    i. Coordinately, unsaturated type (e.g. $-NH_2$, $-S^-$), which contain lone pairs of electrons.
    ii. Coordinately saturated type (e.g. $-^+NH_3$, $-CH_3$).

A free electron model of Platt (1953) is quantitatively satisfying in interpreting the spectroscopic changes cause by introducing the substituents into the basic skeletal structures of molecules. The effects of substituent on aromatic molecule are: the intensification of the power of absorption, obliteration of benzenoids fine structure (for benzene) due to ring vibrational modes and alteration of the shape of the Franck–Condon envelope. The net effect of these in the spectrum is the balance of opposing inductive and resonance effect as submitted by Obi-Egbedi *et al*., (1998). A substituent with lone pair of electron interacts with the electrons of the aromatic ring most effectively under the conditions that the lone pair orbital is parallel to the π-orbital of the aromatic molecule while the alkyl substituents with no lone pair of electron conjugates with the ring through the concept of hyper- conjugation (Lorenc *et al*., 2012).

The conjugation of hydrocarbon nucleus with the phenyl ring has the same effect as amino group on the ring of the molecule, while the presence of substituent like carboxylic group has an opposite effect. The fusion of two or more benzene rings forming a linear or angular compound usually cause bathochromic displacement and in general, with three bands distinguish by their intensities of absorption. This results in greater polarizability and smaller electronic transition energies (Awadesh *et al*., 1988). Klevens and Platt (1942) in their studies, considered spectra relationship among families of substituted aromatic hydrocarbon and proposed that perturbation theory would provide quantitative expression for the prediction of the spectra. Petruska (1961), using the spectra of unsubstituted benzene as the solution to the unperturbed problem assumed that perturbing substituent would mix the various state of the ring with each other and with the intermolecular charge transfer state. This stipulated that a perturbation by several substituents could be expressed as the sum of single substituent perturbation.

$$f = \int \left[\sum_m q_m e^{\left(2\pi i m/3\right)^3} \right]^2 \qquad 2.14$$

where f represents the oscillator strength induced by substituent in the index of the carbon atom of which the substituent is bounded, q_m, the parameter which characterize the substituent at position m, while the exponential term represent the component vectors of the transition dipole of the molecule. The difference between the energy shift of excited state and the energy shift of ground state as considered by Petruska gives the frequency shift as:

$$\Delta\nu = \sum_m l_m + \int \left\{ \sum_m qc_m \left[\sum \nu_m e^{\pi i m/3} \right] \right\}^2 \qquad 2.15$$

where $\Delta\nu$ = red shift of transition frequency. l_m is the first order inductive and second order conjugative shift caused by substituent at position m, $\sum_m$ is the summation over second order mixing term while C_m is the transition coefficient, a measure of relative size of the mixing terms, v_m is the vector parameter which is the character of the constituents at position *m*. The exponential term is the representation in the complex term of the vector addition of second order inductive perturbation. And, for monosubstituted aromatic system, *m= 0* such that equation *2.15* becomes:

$$\Delta \nu = l_m + \sum c_m (\nu_m)^2 \qquad 2.16$$

The theoretical studies of the influence of the substituents on aromatic hydrocarbon by Petruska (1961) and Zenine (1975) indicated that for alkyl benzene and it hydrocarbon, the expression 2.17 holds and this is applicable to other aromatic systems.

$$f_{\text{substituent}} = f_{\text{aromatic molecule with substituent}} - f_{\text{aromatic molecule.}} \qquad 2.17$$

Stevenson (1965), in his extensive studies on the electronic spectra of substituted benzene stressed that the frequency displacements of absorption bands of substituent on benzene molecule are due to electronic interactions of the substituents group with benzene while Burawoy and Thompson (1959), from their studies on substituents effect on the electronic transitions of thio-benzophenone have also shown that the effect of electron donating substituents of groups like -OH, -Ph on the position of K-bands are two folds; the displacement to longer wavelength due to increase in the length of the absorption system as a result of increase in polarizability of the electrons in the terminal group and the increase in polarity of the substituted system which facilitate the electron migration and stability of the excited state. R-bands moves to shorter wavelength on the introduction of the electron donating group because the perturbation resulting from R-band transition extend to the rest of the absorbing system while the reverse order is noted with electron withdrawing substituents. Crowding effects (steric inhibition) has also been observed to cause large blue shift and decrease intensity of absorbance in polar solvents for molecules (Beckette and Stenlake, 1984; Awadesh *et al*., 1988).

Bublitz and Boxer (1997) have also carried out electron absorption (stark) spectroscopy experiment on the donor-acceptor substituted polyenes and discussed the broadening of the absorption spectra with increasing solvent polarity. It was shown that, depending on the solvents, the ground state structure of the solvated molecule can become more or less dipolar, due to the interaction of molecule with the matrix electric field. Changes in the dipole moment and polarizability of the molecules are mirrored by shifts in the position and by broadening of the absorption spectra. The electron withdrawing character of the functional group is expected to stabilize the charge transfer character of the configuration especially in polar solvent. Unlimited number of dyes containing two electron donating group and a simple electron acceptor groups or two electron acceptor groups on the same conjugated system have been reported to have distinctive solvatochromic properties in both absorption and emission (Rezende, 1997; Amrallahah *et al*., 2005). The spectroscopic properties of substituted trans-stilbenes, studied by Gagik and Helmut (2000), where an electron donor and withdrawing groups interact through a π-conjugation of the substituents, was interpreted on the basis of intra-molecular charge transfer (ICT) and the life-time for the decay (deactivation of excited state) was found to be sensitive to solvent polarity.

The studies of Chen *et al*., (1981), from the calculated excited state dipole moment of substituted thiophene have shown a linear correlation with large slope between emission frequency and solvent polarity, suggesting that spectra behaviour of absorption or emission of the compound was related to intra-molecular charge transfer. Moreover, Miralle *et al*., (1997) claimed that the electron withdrawing character of functional groups is expected to stabilize the charge transfer interaction of conjugated molecules especially in polar solvent, with broad and intensed intra-molecular charge transfer absorption band in the visible associated with increase in change in dipole moment ($\Delta\mu$). Lengthening the polyenic chain linking the donor and acceptor molecules result in bathochromic shift of the intra-molecular charge transfer absorption band and induces a linear increase in the excited state moment, but ground state dipole moment remain constant. Earlier studies of Plattner and Heilbronner (1943), using electron withdrawing groups like acetyl and carboxylate have equally shown that blue shift do occur (for the visible band) whenever these substituents are directly attached to five member heteroaromatic ring.

The studies of solvatochromism of aniline and some of its derivatives by Abe's solvatochromic frequency shift theory did not yield reliable values of the excited state electric polarizabilities and dipole moments of molecules. These are not in reasonable agreement with those obtained by means of electro-optical measurement and molecular calculation. The current interest on the derivatives of the O and S five-membered aromatic ring systems, the phenanthrenequinone and cyclopropenone derivatives resolved around the estimation of the change in the dipole moment and polarizabilities by solvatochromic electronic intensity shift method by the application of the rigorous improved formulation of Mc Rae (1950) and Abe (1965) approaches.

2.2 Theoretical treatment of photophysical properties of compounds

This section treats the foundamental theories that form the basis of experimental data treatment in this study.

2.2.1 Electronic intensity in solution and in gaseous media.

The spectroscopic parameters: Oscillator strength (*f*), Einstein coefficient of absorption and induced emission (*k*), the dipole moment (*μ*) and Einstein coefficient of spontaneous emission (*A*) are interrelated such that the use of one depends on the other.

One or more of these parameters; most importantly the oscillator strength and the integral Einstein coefficient of induced absorption or emission (*k*) are use to describe the intensity of optical transitions. The expression for Einstein coefficient and oscillator strength are well defined for electronic spectra intensities in the vapour phase but lack uniformity in solution or condensed media and remains a matter of preference by different authors. The non-uniformity in these expressions as claimed by Iweibo *et al.*, (1982) and Abe and Iweibo (1985b) have been attributed to the existence of two alternative definitions for the experimental and theoretical oscillator strength in solution as previously written in equations 2.6 and 2.7. The observed differences in the definition of oscillator strength was attributed to the variation in the definition of the radiation density (*ρ*), the probability of absorption of molecule per unit time per unit radiation density (i.e the integral Einstein coefficient, k_{ji}) and the choice of the field model. P_{ij} is the probability of absoption per unit time.

$$k_{ji} = \frac{p_{ij}}{\rho} \qquad 2.18$$

The environment alters spectral intensity of the dissolved molecule by altering the charge density and the field acting on the molecule. Thus, k_{ji} varies in definition as a result of variation in the definition of radiation density (ρ) and the field model type used (Liptay, 1966). The radiation densities are variously defined as; the power density ρ at the location of the molecule (i.e $\rho_s = \frac{\varepsilon_r b / E_S^0 /}{8\pi}$), radiation density with respect to the effective field in the condensed medium (i.e $\rho_m = \frac{b / E_S^m /^2}{8\pi}$) and the radiation density with respect to the external field E_o^o (i.e $\rho_0 = \frac{b / E_0^0 /^2}{8\pi}$) on the entire solution where b takes care of the unit of measurement. In S I unit, $b = 4\pi\epsilon_o$ and 1 in cgs unit. ϵ_r is the dielectric constant of the medium relative to that of the vacuum ϵ_0 . These radiation densities are interrelated by the following expressions:

$$\rho_s = \left(\Pi_{i=1}^{r} \beta_{is}\right)\rho_0 = \beta_{is}\rho_m \qquad 2.19$$

$$\rho_v = \left(\Pi_{i=1}^{r} \beta_{iv}\right)\rho_0 \qquad 2.20$$

where $\Pi\beta_{is}$ is the product of the square of the moduli of the solvent correction factors for the different field models, r is an integer whose values depends on the assumed field models. For spherical molecule in the Onsager modified field of Abe and Iweibo (1985b), the components of $\Pi\beta_{is}$ are as defined for various energy levels:

$$\beta_{1s} = n^2$$

$$\beta_{2s} = \left[2 \big/ 1 + n\right]^2$$

$$\beta_{3s} = \left[2n^2 \middle/ 1+2n^2\right]^2$$

$$\beta_{4s} = \left[2n^3 \middle/ 1+n^2\right]^2$$

$$\beta_{5s} = \left[1-\alpha g\right]^{-2}$$

n is the refractive index of the solvent and α is the polarizability of solute while g is the reaction field function which is defined as: $g(n) = \dfrac{2(n^2-1)}{a^3(2n^2-1)}$. It takes the values of *1, 2,* and *3* depending on the molecular shapes of the compound and $a > 0$. Due to the parameters defined above, the expressions for the correction factors for the various field models (Lorentz, Onsager, Onsager–Botcher and the modified Onsager–Botcher field models) vary considerably (Iweibo *et al.*, 1990). Also, base on the radiation densities specifications, absorption probability and their corresponding Einstein probability coefficient of absorption take the form:

$$p_{ij}(\rho_q) = k_{jis}(\rho_q)\rho_q \qquad 2.21$$

where "*q*" may be replaced by *o, s, m or v* for the particular radiation density under consideration. From these, the variant for the definition of oscillator strength in term of the ratio of the Einstein probability coefficient of absorption in solution to the vapour phase harmonic oscillator is as expressed in equation *2.22*:

$$f_{jis\rho s} = \frac{p_{jis}(\rho_s)}{p_{jivh}(\rho_v)} = \frac{k_{jis}(\rho_s)\rho_s}{k_{jivh}(\rho_v)\rho_v} \qquad 2.22$$

This expression, according to Abe and Iweibo (1985b) and Iweibo *et al*., (1990) is most preferred fundamental definition of oscillator strength that allows for comparison of data determined in different solvents.

2.2.2 Experimental and theoretical expression for oscillator strength

By applying the Bouguer-Lambert-Beer's law to a microscopic of molecules randomly oriented in a condensed medium of volume *V* and radiated with light propagating along the z–coordinate, the Bouguer-Lambert-Beer relationship of equation *2.23* and *2.24* holds.

$$I_{sl} = I_{so} \exp\left[-(\ln 10)V \frac{N}{N_0} \varepsilon_{(v)s} l\right] \qquad 2.23$$

$$I_{sl} = I_{so} \exp\left[\frac{n}{c} k_{jis}(v,\rho) Nhvl\right] \qquad 2.24$$

In these equations, I_{so} is the intensity of the incident radiation on the solution surface, I_{sl} is the transmitted intensity at the solution surface, $\varepsilon_{(v)s}$ is the molar absorptivity at frequency v for the entire solution and it incorporates the effects of interaction of solute and the exciting field with the solvent, N is the number of molecules per unit volume, while N_o the Avogadros number and l the optical path along the coordinates. Equation *2.24* defines I_{sl} in term of the differential Einstein's coefficient $k_{jis}(v,\rho)$. The intensities I_{so} and I_{sl} cannot be measured with accuracy in practice because of reflection losses at the solution boundaries, intensity modification by the cuvette and the convenient placement of the photo detector in air rather than at the solution boundaries. To overcome these problems, most modern quantitative spectrophotometers with double beam optics are made for measurement of absorbance. Thus, the ratio of the intensity in the reference cell to that in the solution gives:

$$A = \log_{10}\left(\frac{I_{slr}}{I_{sl}}\right)_v = V\left(\frac{N}{N_0}\right)\varepsilon_{(v)s} l \qquad 2.25$$

This may be transformed to give:

$$A = \log_{10}\left(\frac{I_{slr}}{I_{so}}\right)_v + \log_{10}\left(\frac{I_{so}}{I_{sl}}\right)_v = V\left(\frac{N}{N_0}\right)\varepsilon_{(v)s} l \qquad 2.26$$

The measured absorbance as given by the equation *2.24* where I_{slr} is the transmitted intensity by the reference solvent at any point in the cuvette and $\varepsilon'_{(v)s}$ is the molar absorptivity of the solvent-perturbed solute isolated from the rest of the surroundings is regarded to be related to the macroscopic quantity; Einstein coefficient $k_{jis(v,\rho),}$ where $k_{jis(v,\rho),} = \int k_{jis}(_{v})d\,v$. In the vapour phase where the environment of the solute is a vacuum, $I_{slr} = I_{v0}$ and $\varepsilon_{(v)} = \varepsilon'_{(v)s}$ Iweibo *et al*., (1990).

By re- expressing the left hand side of equation *2.26* as: $\log_{10}\left[\left(\mathrm{I_{so}}/\mathrm{I_{sl}}\right)\times\left(\mathrm{I_{slr}}/\mathrm{I_{so}}\right)\right]$, this equation is transformed into:

$$\varepsilon_{(v)s} = \varepsilon'_{(v)s} + \varepsilon''_{(v)s} \qquad 2.27$$

$$\text{where } \varepsilon'_{(v)s} = \frac{1}{V\left(N/N_0\right)l}\log\left(\frac{I_{so}}{I_{sl}}\right)_v \quad \text{and } \varepsilon''_{(v)s} = \frac{1}{V\left(N/N_0\right)l}\log\left(\frac{I_{slr}}{I_{so}}\right)_v$$

And, the second summand in equation 2.27 is given by:

$$\varepsilon''_{(v)s} = \frac{1}{c'(\ln 10)l}\ln\left[\frac{(1+n(v))}{4n(v)}\times\left(1+d^2-2d\cos(2Kl)\right)\right] \qquad 2.28$$

where I_{so}/I_{slr} is the quantity in the square bracket in equation 2.28 and is obtained from a consideration of the modification of the field intensity of the exciting light as it transverses the three layer structure: air-solvent-air. The symbol K is the wave vector in the solvent, $d = \left(\frac{\mathrm{n}(v)-1)}{\mathrm{n}(v)+1}\right)^2$, n is the real part of the refractive index while $c' = V\,N/N_o$.

In band intensity form, integrating equation *2.27* over all the frequency and noting that $\int_0^{\alpha}\ln\left[1+d^2-2d\cos(2kl)\right]dv = 0$ change it to:

$$\int \varepsilon_{(v)s}\,dv = \int \varepsilon'_{(v)s}\,dv + \frac{1}{c'(\ln 10)l} \times \int \ln\left[\frac{(1+n(v))^2}{4n}\right]_v dv \qquad 2.29$$

where $(1+n(v))^2 / 4n$ represents Abe-Iweibo's correction factor for refraction effect at the solution interface (Abe and Iweibo, 1985b). Also, from equation *2.29* and Bouguer-Lambert-Beer law, the experimental Einstein's coefficient for the radiation density of the solvated solute molecule, $k^{\exp}_{jis}(\rho_0)$ was obtained from the relationship between the $\varepsilon_{(v)s}$, the Einstein coefficient (k_{jis}), the amount of energy ($W_{(v)} = \rho_s\,dv = Nhv$) absorbed at a given frequency of radiation by molecules in an element of volume *dv*,and unit time $dt = ndz/c$ as:

$$\log_{10} I_{so}/I_{sl} = \left(n/c\ln 10\right) k_{jis}(v,\rho_0) Nhv_{jis} l = V\left(N/N_0\right)\varepsilon_{(v)s} l \qquad 2.30$$

Hence, $k_{jis}(v,\rho_o) = (\ln 10)\,Vc/N_0 hn \int \varepsilon_{(v)s}\, dv/v$ $\qquad$ *2.31*

Similarly, its vapour phase expression for harmonic oscillator in an allowed transition is:

$$k^{\exp}_{jivh}(\rho_0) = \frac{\pi e^2}{bmhv_{jivh}}\left\{\frac{\Pi\beta_{iv}}{\beta_{iv}}\right\} \qquad 2.32$$

These expressions of *k* and *f* which are based on field models of Lorentz, Onsager and Onsager- Bottcher assumed the cavity to be emptied. Under this assumption,

$$\left\{\frac{\Pi\beta_{iv}}{\beta_{iv}}\right\} = 1$$

Also, the expressions neglected completely the $\varepsilon''_{(v)s}$ component of $\varepsilon_{(v)s}$ of equation *2.27*. These two assumptions, using the correlation of $f_{jis\rho 0} = \dfrac{k_{jis}(\rho_0)\rho_0}{k_{jivh}(\rho_0)\rho_0}$ reduce equations *2.8* and *2.9* to equations *2.33* and *2.34* respectively.

$$f_{jis\rho_0}^{\exp t} = (\ln 10)\frac{Vmb}{N_0 h\pi e^2}\left\{\frac{\beta_{1v}}{n\prod\beta_{1v}}\right\}v_{jiv}\int\varepsilon_{(v)s}\frac{d\bar{v}}{\bar{v}} = (\ln 10)\frac{Vmb}{N_0 h\pi e^2}v_{jiv}\int\varepsilon_{(v)s}\frac{d\bar{v}}{\bar{v}} \qquad 2.33$$

$$f_{jis\rho_0}^{theor} = \frac{8\pi^2 m}{3he^2}v_{jiv} / \mu'_{jis} /^2 \frac{\prod \beta_{is}/\beta_{1s}}{\prod \beta_{iv}/\beta_{1v}} \qquad 2.34$$

On comparing these expressions, it was found that the equations has two major advantages relative to the previous derivations, in that equations *2.33* provides in terms of $\varepsilon^{//}{}_{(v)s}$, the experimental correction arising from the optics of double beam absorption meters and both equations i.e *2.33* and *2.34* extend to models in which the cavity is not empty but is filled with the materials of the solute and or solvent and also accommodate systems in which the molecular dimensions and internal field functions of the solute differ in the vapour and solution phases (Iweibo *et al*., 1990).

2.2.3 Modification of charge density and solvent enhancement of intensity borrowing

The dipole moment for solution of molecule is the sum of the dipole moment for the solute molecule (μ_a) and that of the solvent molecule (μ_b) (Bayliss, 1969).

$$\mu = \mu_a + \sum_{j=1}^{N}\mu_b \qquad 2.35$$

Thus, the total wave function of the solution is the product of the wave function of solute and that of the solvent. Using the first order perturbation theory, the transition of an electron from ground state α_o to the first excited state α_i in the solution has the wave function for the ground and excited state as written in equation *2.36* and *2.37*.

$$(\alpha\beta)_{so} = \alpha_0\beta_0 + \sum_{p\neq 0} c_{p000}\alpha_p\beta_0 + \sum_{q\neq 0} c_{0q00}\alpha_0\beta_q + \sum_{p,q\neq 0} c_{pq00}\alpha_p\beta_q \qquad 2.36$$

$$(\alpha\beta)_{si} = \alpha_i\beta_0 + \sum_{p\neq i,q\approx 0} c_{pqi0}\alpha_p\beta_q + \sum_{p\neq 0} c_{p0i0}\alpha_p\beta_0 + \sum_{p,q\neq 0} c_{iqi0}\alpha_i\beta_q \qquad 2.37$$

The general perturbation coefficient c_{pqi0} is: $\dfrac{\left\langle \alpha_p \beta_q / \mathrm{V}' / \alpha_i \beta_m \right\rangle}{\left(E_{ap}^{\alpha} + E_{bq}^{\beta}\right) - \left(E_{ai}^{\alpha} + E_{b0}^{\beta}\right)}$

$$V' = \iint \frac{\rho_\alpha(r_\alpha) \times \rho_\beta(r_\beta)}{/ r_\alpha + r_\beta /} \delta r_\alpha \delta r_\beta \qquad 2.38$$

where V' is the perturbation Hamiltonian for interaction energy, with E being the perturbed energy of a given state p and q of the solute and the solvent respectively. These equations are relevant for the development of the frequency shift equations. In these equations, α is the wave function of the solute while β is the wave function of solvent molecules with which the solute interacts while o and ί refer to the ground and excited state notation. $\rho_\alpha(r_\alpha)$ and $\rho_\beta(r_\beta)$ as defined by Longuett–Higgins and Salem (1961) are the operator for the charge density ρ at the position vector r_α and r_β for the solute molecule (α) and the solvent molecule (β) respectively According to Bayliss (1969), to describe the intensity borrowing modes from solvent phenomenon, the transition moment integral in the solvent is as described by equation *2.39*:

$$\langle(\alpha\beta)_{si}|\mu|\,(\alpha\,\beta\,)_{so}\rangle = \langle((\alpha_i\beta_o + \sum_{p\neq i,q\neq o} C_{pqio}\alpha_p\beta_q|\mu|\alpha_i\beta_o + \sum_{p,q\neq o} C_{pqoo}\alpha_p\beta_q))\rangle \qquad 2.39$$

where $\mu = \mu_\alpha + \mu_\beta$ is the dipole unit operator. By imposing orthogonality of wave function in different states, by expanding and simplication of equation *2.39* and neglecting terms with double summation or term with coefficient *c²* and CC, it yields the non-vanishing terms described by equation *2.40*. This is because the denominator of each C term is much larger than its numerator and the coefficient *c²* and CC contribute virtually little or nothing to the C terms. Thus,

$$\begin{aligned}\langle(\alpha\beta)_{si}|\mu|\,(\alpha\,\beta)_{so}\rangle = {} & \langle\alpha_i|\mu_\alpha|\alpha_o\rangle + C_{iooo}\{\langle\alpha_i|\mu_\alpha|\alpha_i\rangle - \langle\alpha_o|\mu_\alpha|\alpha_o\rangle\} \\ & + \sum_{p\neq o} C_{pooo}\langle\alpha_i|\mu_\alpha|\alpha_j\rangle + \sum_{q\neq 0}\left(c_{iqoo} + c_{oqi0}\right)\left\langle\beta_o|\mu_\beta|\beta_q\right\rangle \\ & + \sum_{p\neq i} C_{poio}\langle\alpha_p|\mu_q|\alpha_o\rangle \qquad 2.40\end{aligned}$$

The first term of equation *2.40* is the transition moment for isolated (unperturbed) solute. The second term describes the contribution from the change in permanent dipole moment of the solute during the transition $\alpha_0 \rightarrow \alpha_i$ (i.e dipole moment between the ground and the forbidden transition of the excited state of the molecule otherwise called Stark term). The third term is the contribution from the static field of the perturber while the fourth terms describe how the transition moment of the perturbed solute borrows intensity from the transitions of the solvent (i.e. the contribution from higher excited state), and the fifth term is the contribution from electronic transitions of the solvent molecules (the dispersion term involving the forbidden transition density and that of the electron density of $\beta_0 \rightarrow \beta_i$ transition of solvent). These terms indicate that the intensity borrowing is possible from electronic transition in the solvent through scrambling of the electronic states of molecules by interaction with perturbing solvent molecules and or from electronic transitions in the solvent $(\alpha_0 \rightarrow \alpha_i)$ (Obi-Egbedi, 1996).

2.2.4 Expressions for determining the molecular transition polarizabilities and transition dipole moments.

Recall that the existing Abe-Iweibo's Solvatochromic Shift Equation of equation 2.13 is given by:

$$hv_{(s)} = hv_{(v)} - \left\{ \frac{2}{3} \frac{\left(\mu^{*2}_{a} - \mu_a^2 \right)}{dkT} + \left(\alpha_a^{\,*} - \alpha_a \right) \right\} \sum_{i=1}^{N} \frac{\mu_{bi}^2}{dr_{abi}^6} - \frac{\left(\mu^{*2}_{a} - \mu_a^2 \right)}{d}$$

$$+ \frac{3}{2} \left[\frac{\alpha_g^* I_g}{1 + \frac{I_g}{I_g^*}} - \frac{\alpha_g I_g}{1 + \frac{I_g}{I_e^*}} \right] \sum_{i=1}^{N} \frac{\alpha_g}{r_{abi}^6}$$

The inherent large spread in the dipole moment and polarizability of molecules in the ground and excited state reported using this equation (2.13) led to its modification following the treatment of Longuett–Higgins and Salem (1961) definition of the electrostatic interaction energy.

The interaction of solute photon absorber with solvent molecules can yield useful information on the photo-physical properties of the solute; such as the dipole moment, polarizability, energy and molecular structures. The properties of solvated solute can be correlated to that of the vapour state whose determination may not be experimentally feasible and to identify the terms that contribute to the oscillator intensity parameters in solution. In the transition from the ground state to the excited state, the interaction between the solute transition moment and that of the solvent; the interaction between the transition polarizability and the static field of the solvent are the origins of the intensity enhancement, apart from that due to the transition moment of the isolated molecule.

Therefore, to quantify the perturbation of the transition energy or frequency of solute molecule immersed in solvent, quantum mechanical perturbation theory is used (Iweibo *et al*., 1991). By permitting the total Hamiltonian operations H_s (*2.41*) to act on the ground and excited states wave functions of any system (solute and the solvent), and following the treatment of Longuett–Higgins of equation *2.38* as stipulated by Bayliss (1969), the detailed expression for the interaction energy operator H_s is the expression of the electrostatic interaction between the charge distribution of the solute (A) and the solvent (B).

$$H_s = H_a + H_b + V' \qquad 2.41$$

where H_a and H_b are the functions of electronic and nuclear coordinates of the solute and the perturber (solvent) respectively, V' (the perturbation Hamiltonian for interaction energy operator), is a function of molecules A and B, the distance between them and their mutual orientation. The distance between A and B is assumed to be a weak and is such that no electron exchange can occur between the solute and solvent. The zero-order wave function of the system can then be adequately described by the orthogonal set of product wave functions, $\alpha_i B_q$, which are solutions of the Schrodinger equation. The effect of solute-solvent interaction V', is that the zero-order wave function, described by $\alpha_i \beta_q$, is modified by the perturbation to the form of equation *2.40* as:

$$\begin{aligned}\langle(\alpha_i\beta_o)_s|\mu_a+\mu_b|(\alpha_o\beta_o)_s\rangle &= \langle\alpha_i\beta_o|\mu_a+\mu_b|\alpha_o\beta_o\rangle+\sum_{p\neq o}C_{poo}\langle\alpha_p\beta_o|\mu_a+\mu_b|\alpha_i\beta_o\rangle \\ &+\sum_{p\neq o,q\neq o}C_{pkoo}\langle\alpha_p\beta_q|\mu_a+\mu_b|\alpha_i\beta_0\rangle+\sum_{q\neq o}C_{oqoo}\langle\alpha_o\beta_q|\mu_a+\mu_b|\alpha_i\beta_o\rangle \\ &+\sum_{p\neq i,q\neq o}C_{poio}\langle\alpha_p\beta_o|\mu_a+\mu_b|\alpha_o\beta_o\rangle+\sum_{p\neq i,q\neq 0}C_{pqio}\langle\alpha_p\beta_q|\mu_a+\mu_b|\alpha_o\beta_o\rangle \\ &+\sum_{q\neq o}C_{iqio}\langle\alpha_i\beta_q|\mu_a+\mu_b|\alpha_o\beta_o\rangle\end{aligned} \qquad 2.42$$

The general perturbation coefficient C_{pqi0} as previously expressed is proportional to the electrostatic interaction between the charged distributions of the solute (α) and the solvent (β) and inversely proportional to the sum of the transition energies of the perturbed solute and the solvent. And, following the treatment of Longuett–Higgins and Salem definition of equation *2.38*, the detailed expression for the interaction energy operator V' is the expression of the electrostatic interaction between the charge distribution α and β expressed in *2.43*. In expanding each perturbation coefficient C term in equation *2.42* and solve them in terms of molecular properties and Longuett-Higgins' rigorous definition of the electrostatic interaction energy, the Hamiltonian operator (V') was approximated as:

$$V' = -\frac{\mu_\alpha\mu_\beta k_{\alpha\beta}}{br_{\alpha\beta}^3} - \frac{1}{2}\left(\frac{\mu_\beta\mu_\beta k_{\beta\beta}}{br_{\beta\beta}^3}\right) \approx -\frac{\mu_\alpha\mu_\beta}{r_{\alpha\beta}^3} \qquad 2.43$$

This permits the solution of the coefficient term to:

$$\sum\nolimits_{p\neq 0} c_{p0i0}\mu_{ap0} = \frac{\langle\alpha_p\beta_q/V'/\alpha_i\beta_m\rangle}{\left(E_{ap}^{\alpha}+E_{q0}^{\beta}\right)-\left(E_{ai}^{\alpha}+E_{b0}^{\beta}\right)} = \sum\nolimits_{p\neq 0}\frac{\mu_{api}\mu_{apo}}{\Delta E_{api}}\frac{\mu_{boo}}{r_{\alpha\beta}^3} \qquad 2.44$$

where $r_{\alpha\beta}$ is the sum of the radii of the position vector of the solute and that of the solvent molecules, μ_α and μ_β are the dipole moment of the solute and solvent molecules respectively, $r_{\alpha\beta}$ is the internuclear distance (the sum of the radii of the position vector) of the solute and the i^{th} solvent molecule, $k_{\alpha\beta}$ is a geometrical factor which depend on the mutual orientation and separation of the two dipole while b = $4\pi\varepsilon_o$, ε_o being the vacuum permittivity. All molecules are rigid and fixed in position and orientation; therefore, statistical averaging is performed over all molecular orientations and assuming Boltzmann's distribution.

Therefore, by analysis of each term on the right-hand side of equation *2.42*, many terms or components of terms vanish by virtue of the orthogonality of the wave functions in the overlap integrals that multiply such terms. Under this condition equation *2.42* reduces to equation *2.45*.

$$\langle(\alpha_i\beta_o)_s|\mu_a+\mu_b|(\alpha_o\beta_o)_s\rangle = \mu_{aio(v)} + \sum_{p\neq o} C_{poio}\mu_{api} + \sum_{p\neq i} C_{poio}\mu_{apo} + \sum_{q\neq o} C_{oqio}\mu_{bqo} + \sum_{q\neq i} C_{iqoo}\mu_{bqo} \qquad 2.45$$

In equation *2.45*, the notation has been simplified such that μ_{aio} = $\langle\alpha_i|\mu_a|\alpha_0\rangle$ which is the transition moment of the solute from state $\langle\alpha_0|\mathit{to\ state}|\alpha_i\rangle$.

Further analysis is simplified by pairing the solved terms of equation *2.45*, namely; terms two and three on one hand and terms four and five on the other hand such that the expression in *2.46* holds.

$$|\mu_{aio}|_s = |\mu_{aio}|_v + \left(\frac{2\Delta E_{bqo}\Delta E_{aio}|\mu_{\alpha io}|}{(\Delta E_{bqo}^2 - \Delta E_{aio}^2)r_{\alpha\beta}^3}\right)\left(\frac{\sum_{q\neq 0}|\mu_{bqo}|^2}{\Delta E_{bqo}}\right) + \left(\sum_{p\neq i}\frac{\mu_{\alpha pi}\mu_{\alpha po}}{\Delta E_{\alpha pi}} - \sum_{p\neq q}\frac{\mu_{\alpha po}\mu_{\alpha pi}}{\Delta E_{apo}}\right)\frac{\mu_{boo}}{r_{\alpha\beta}^3} \qquad 2.46$$

Dividing and multiplying the second term on the right-hand side of equation *2.46* with *3/2* and ΔE_{bko}^{2}, equation *2.47* is obtained.

$$\left|\mu_{ai0}\right|_s = \left|\mu_{aio}\right|_v + \left[\frac{3\left|\mu_{aio}\right|_s \, \Delta E_{\alpha io}}{\left(1-\dfrac{\Delta E_{aio}^{2}}{\Delta E_{bqo}^{2}}\right)\Delta E_{bq0}}\right]\left[\frac{2 \ \sum_{q\neq o}\left|\mu_{bqo}\right|^{2}}{3 \ \Delta E_{bqo} r_{\alpha\beta}^{3}}\right] + \left(\sum_{p\neq i}\frac{\mu_{\alpha po}\mu_{\alpha pi}}{\Delta E_{api}} - \sum_{p\neq o}\frac{\mu_{api}\mu_{apo}}{\Delta E_{apo}}\right)\frac{\mu_{boo}}{r_{\alpha\beta}^{3}} \qquad 2.47$$

From equations *2.46* and *2.47*, μ_{aio} and μ_{bko} are the transition moment of the solute and solvent respectively. ΔE_{aio} is the transition energy or ionization potential of the solute while ΔE_{bko} is the corresponding ionization potential for the solvent molecule. The third term (in the circular brackets) is the transition polarizability (Δα) as defined by Labhart (1961) and Donath (1961) formalism. By multiplying the equation through with the Eistein coefficient (k_{jis}) and by equating $k_{jis}\ \mu_{aio}$ to $f_{aio}^{\frac{1}{2}}$, equation *2.47* is transformed into *2.48*:

$$f_{aio(s)}^{\frac{1}{2}} = f_{aio(v)}^{\frac{1}{2}} + \frac{3x}{1-x^{2}}\, f_{aio(v)}^{\frac{1}{2}}\left(\frac{\alpha_b}{r_{ab}^{3}}\right) + \Delta\alpha \mathrm{k}_{\mathrm{jis}}\left(\frac{\mu_{b00}}{r_{\alpha\beta}^{3}}\right) \qquad 2.48$$

$f_{aio\,(v)}^{1/2}$ is the root of the oscillator strength in the vapour phase and $f_{(s)}^{1/2}$ the root of the oscillator strength in the solution phase, x is the ratio of the ionization energies of the absorbing solute to that of the solvent molecules, i.e $x = \dfrac{\Delta E_{aio}^{2}}{\Delta E_{bko}^{2}}$, $\Delta E_{aio}^{2} > \Delta E_{bko}^{2}$ and ΔE_{bko}^{2} $\neq 0$. Equation *2.48,* whose consistency is being tested in this research, is the modified form of Abe-Iweibo Solvatochromic Shift Equation (SSE) of equation *2.13*. For the purpose of this study, equation *2.48* is rearranged into the linear regression forms of equations *2.49* and *2.50* as:

$$\frac{f^{\frac{1}{2}}_{aio(s)} - f^{\frac{1}{2}}_{aio(v)}}{X_1} = \frac{3xf^{\frac{1}{2}}_{aio(v)}}{1-x^2} + \Delta\alpha k_{jis}\frac{X_2}{X_1} \qquad 2.49$$

$$f^{\frac{1}{2}}_{aio(s)} = f^{\frac{1}{2}}_{aio(v)}\left(1+\frac{3x}{1-x^2}X_1\right)+\Delta\alpha k_{jis}\left(X_2\right) \qquad 2.50$$

The dependent variables are $\frac{f^{\frac{1}{2}}_{aio(s)} - f^{\frac{1}{2}}_{aio(v)}}{X_1}$ and $f^{\frac{1}{2}}_{aio(s)}$ in equations *2.49* and *2.50* respectively; while the independent variables are $k_{jis}\frac{X_2}{X_1}$ and $f^{\frac{1}{2}}_{aio(v)}$ in equations *2.49* *2.50* respectively. These two equations satisfy the statistical criterion for regression or graphical analysis in this research and the slope gives the value of Δα from equation *2.49* while Δα is obtained from the intercept in equation *2.50*. The value of Δα determined is slotted into the expression in *2.51* to determine the transition dipole moment (Δμ).
Equation *2.51* was also obtained by expansion of equations *2.36* and *2.37* and following the treatment of Longuett–Higgins and Salem definition of equation *2.38*.

$$f^{\frac{1}{2}}_{(aio(s)} = \Delta\mu + \frac{3}{2}\Delta\alpha\left(\frac{\mu_{boo}}{r^3_{ab}}\right) + \left(\frac{3x}{1-x^2}\, f^{\frac{1}{2}}_{aio(v)}\, k_{jis}{}^{-1}\right)\frac{\alpha_b}{r^3_{ab}} \qquad 2.51$$

The modified SSE (Equations *2.48* and *2.51*), developed from the intensity perturbation approximation has incoorporated in them intensity parameters: Einstein coefficient (k_{jis}), stark term ($\frac{\mu_{b00}}{r^3_{\alpha\beta}}$), oscillator strength (*f*) in solution and vapour phases, solute molecular ground state polarizability(α_g) and the molar refraction (*R*) while the Abe-Iweibo Solvatochromic Shift Equation of *2.13* incoorporated in it the energy terms for molecules in solution [$hv_{(s)}$] and vapour [$hv_{(v)}$] phases.

2.2.5 Shapes of absorption bands

The intensity of a transition as seen in equation *2.1* is proportional to the square of the modulus of the transition moment. Vibrations within molecules alter the transitions from ground state to the excited state through;

a. The changes in the equilibrium position of the states involved i.e. $r_{eq}^{*} \neq r_{eq}^{0}$

b. The changes in the potential energy surface in the different states i.e $\frac{\partial E_{(r)}^{*}}{\partial r} \neq \frac{\partial E_{(r)}^{0}}{\partial r}$

where r_{eq}^{*} and r_{eq}^{0} are the equilibrium positions in the excited and ground state respectively. According to Heisenberg, it is impossible for the energy to be determined at exactly the time of transitions. Thus, the intensity of absorption can be expressed as:

$$I \propto /\mu_{ji}\,(r_{eq})/^{2} = \sum_{i=0}\ /<\psi_{ji}\,(r)\mu_{io}\,(r)>/^{2} \qquad 2.52$$

where ψ is the vibrational wave function, i and j are the ground and excited state electronic levels, i and o are the vibrational quantum number for the excited and ground state respectively. The changes in the equilibrium position (distance) and potential energy surface determine the shape of the absorption band (Lesi, 1996).

i. If there is no change in the potential energy surface i.e $r_{eq}^{*} = r_{eq}^{0}$ and $\frac{\partial E_{(r)}^{*}}{\partial r} \neq \frac{\partial E_{(r)}^{0}}{\partial r}$

   During transitions from ground to excited state, the o–o transition will be highly intensed and the symmetry of the ground and the excited state ψ_{ji} and ψ_{io} will be the same, but ψ_{ji} and ψ_{io} may have different symmetries i.e 1–1, 2–2 transition will occur as hot bands.

ii. The transitions from zero to even number states will be allowed while the transitions from zero to odd number states will be forbidden if the equilibrium distance is not the same for the potential energy surface changes i.e ($r_{eq}^{*} \neq r_{eq}^{0}$) and $\frac{\partial E_{(r)}^{*}}{\partial r} \neq \frac{\partial E_{(r)}^{0}}{\partial r}$ for simple molecules.

iii. If the equilibrium bond length changes from the ground to the excited state, i.e $r_{eq}^{*} \neq r_{eq}^{0}$, vibrational structure is observed in the spectrum. Also, large and small displacements from equilibrium positions are seen as symmetrical and as asymmetrical band structure respectively. But, for poly atomic molecules, if there is no change in symmetry from the ground to the excited state, only total symmetric vibrations will contributes to the progression (Lesi, 1996).

2.2.6 Theoretical treatment of substituent effect on oscillator strength, transition moment and intensity

The theoretical study of the influence of groups or subtituents on the position and the intensity of the electronic transition of hydrocarbons or hetero-hydrocarbon moeties allow one to obtain information concerning their structures (Nicholae, 2002; Natasa *et al*., 2006). The remarkable results obtained from the characteristic of the electronic spectra; absorption band profile, absorption coefficient and absorption frequency offer the strength of oscillator which characterized the absolute intensity and the width of the absorption bands. The main modes of action of the substituents on the shift in the position and intensity of absorption are governed by:

i. The resonance or mesomeric interaction with the ring or skeleton of the unsaturated bond by its ability to extend space over which π-electrons of the molecules are delocalized; this directly depend on the energy and the size of the orbitals of appropriate π-symmetry of the substituents. The substituent which occupies orbital of relatively high energy acts as electron donor while those with empty orbital of low energy will function as electron acceptor.

ii. The polarity of the ring substituents bonds (Inductive or transmission effect) which alters the potential field in the π-electrons of the parent compounds may also modify their energies.

iii. The difference in spatial extent of the resonating chain in cis and trans- isomers.

iv. The crowding effects of the substituents (steric inhidrance) on the atoms in the conjugated chains which relatively cause deviation from polarity of atoms in the chain

One or any combination of these effects may be dominant in the spectroscopic manifestation of the effect of substituents, and the over all substituents effect depend not only on the type and number of substituents but also on the position of substituents in the aromatic ring and the nature of the transitions involved (Lees and Burawoy, 1964; Natasa *et al.*, 2006).

Factors i, ii and iii are important for substituents at the C_2 and C_5 position of the N, O and S five member ring hetero aromatic systems while for substituents at both C_2 and C_3 position of the highly strained cyclopropenone ring and C_3 or C_4 position of the substituted heterocyclic systems, inductive and steric effects are of more importance (Finar, 1973; Gilchrist, 1992). Linear or angular condensed ring hydrocarbon are usually accompany by steady increase in the wavelength of absorption maximum and the absorption intensity with increase in ring systems due to factor (i). And, the introduction of substituents into the ring causes modification of the basic absorption due to changes in the spatial orientation of the electronic transition (Hu *et al*., 2011; Praveen and Ojha, 2012).
It has been established that the ultraviolet spectra of the substituted aromatic molecules contain the same electronic transitions as the spectrum of its unsubstituted molecule but with shift in frequency and intensity (Doub and Vanderbelt, 1955). To develop the theory of substituents effect on aromatic ring, using benzene as model, the following assumptions are usually made by incorporating the ideas of Skalar (1942) and Platts (1951).

i. The carbon ring is undistorted on substitution.
ii. The substituents replacing the H atom in the aromatic molecule is symmetric with respect to reflection at the plane of the ring.
iii. The carbon substituents bonds are the same for poly substitution as for mono substitution as there is no interaction between the substituents.

The substituents perturbation operator P is the sum of the perturbation operator for monosubstitution (P_m) i.e $P = \sum_m P_m$. The transition frequency in aromatic and hetero aromatic molecules from the ground to excited state changes because of the interactions of the configurations and energy state with one another and with substitution, and with charge transfer state. Aromatic compounds show a number of bands and in Platts notation, these are $^1A \rightarrow {}^1L_b$, $^1A \rightarrow {}^1L_a$ and $^1A \rightarrow B_{ab}$ with $^1B_{ab}$ state been doubly degenerate for certain symmetric derivatives, but splits for nearly all substituted aromatic molecule (Platts, 1951; 1953). For unsubstituted furan and thiophenes, two prominent bands are usually observed with carbon atom at position 2 (or 5) having large electron densities than those at 3 (or 4) position in five-membered heteroaromatic compounds (Finar, 1973).

Assuming ψ is the state function for the various electronic states of the carbon ring, ψ_o and ψ_i represent the ground and the excited states wave function respectively and ψ_m is the state function for various excited electronic states of the substituents at position m of the molecule. The charge-transfer state is obtained by transferring electron from the heterocyclic atom or carbon ring to the substituent or vice-versa.

By adopting the ideal of Petruska, 1961, the electronic transitions of substituted furan, thiophene and phenanthrenequinone are regarded as being derived from transitions of their parents compounds (furan, thiophene and phananthrene) respectively. Thus, changes in the intensities and energies of the transitions are caused by:

i. Inductive perturbation in which the substituents cause the states of the parent compounds being studied to mix with each other.

ii. Conjugative perturbation in which these compounds states mix with the states which comes about through the introduction of the extra π-electrons and the orbitals of the substituents. These treatments assume that the substituents effects are small enough to be described by perturbation theory.

In this theory, the following types of matrix element occurs i.e.

$$P^{x\lambda} = \langle R^x | P | R^\lambda \rangle \qquad 2.53$$

$$P_m^{k\lambda} = \langle R^x | P | S_m^\mu \rangle \qquad 2.54$$

where R^x and R^λ are the two states of these molecules (i.e. ground and excited state). $S_m{}^\mu$ is a substituent state characteristic of the group and m is the position of the substituent while P is the operator representing the substituent perturbation. When there are two or more substituents, $P^{x\lambda}$ is a vector sum on the complex plane of the separate contributions of the substituents, and the vector dependence are to be determined from the group theoretical properties of the molecules. The state functions are transformed in, so that they are oriented towards the position of substitution in order to perform the summation of mono substitution indicated for the width of a band whose oscillator strength value is given by the correlation:

$$f_{(s)} = \frac{2.303 m_e c^2 \varepsilon_o}{N_0 e^2 n} \int_{vi}^{vj} \varepsilon_{\bar{\upsilon}}\, \partial \bar{\upsilon}_j \;=\; \frac{4.321x10^{-9}}{n} \int_{vi}^{vj} \varepsilon_{\bar{\upsilon}}\, \partial \bar{\upsilon}_j \qquad 2.55$$

where ε_v is the molar coefficient of extinction for the radiation with the frequency ν with ν_i and ν_j being the field of the spectra bands.(Iweibo *et al*., 1990; Nicolae, 2002).

To describe the changes produced by ideal substituent perturbation in the dipole moment and transition probability, the ground and excited state wave functions described by (ψ_o and ψ_i) are considered. This changed by an amount $\Delta\psi_o$ and $\Delta\psi_i$ respectively. Also, the corresponding transition probability or dipole strength measuring the intensity of transition changes by $\Delta\mu$ and ΔI_o respectively (Milliken and Reike, 1941, Phillip, 1965). These are as represented in equations 2.56 and *2.57*

$$\Delta\mu_{0i} =< \Delta\psi_0/r/\psi_i > +< \psi_0/r/\Delta\psi_i > \qquad 2.56$$

$$\Delta I_{0i} =/\mu_{0i} + \Delta\psi_0/^2 -/\psi_{0i}/^2 = 2\mu_{0i}\Delta\psi_{0i} +/\mu_{0i}/^2 \qquad 2.57$$

2.3 Computational chemistry and its features

Computational chemistry is a branch of chemistry that applies mathematical and theoretical (quantum) principles to solve chemical problems using efficient computer programmes into which the results of theoretical chemistry have been incorporated (Young, 2001 and Gece, 2008). This is an exciting and fast-emerging discipline which deals with the modelling and computer simulation of systems such as bio-molecules, polymers, drugs, inorganic and organic molecules. Since its advent, computational chemistry or quantum chemical methods have proven to be very useful in determining the molecular structure, as well as, elucidating the electronic structure and reactivity of chemical systems. As such, it has become very popular, being of immense benefit as a result of tremendous improvements in computer hardware and software. With high computing power using parallel or grid computing facilities and with faster and efficient numerical algorithm, it is being effectively used to solve complex chemical and biological problems (Gece, 2008 and Ramachandran *et al*., 2008).

Computational chemistry is used in a number of ways. One particular important way is to model a molecular system prior to synthesizing it in the laboratory, which is often good enough to rule out 90% of possible compounds as being unsuitable for their intended use. This is very useful information because synthesizing a single compound could require months of labour and raw materials, and generate toxic waste. A second use of computational chemistry is in understanding a problem or experimental data more completely (Young, 2001; Ramachandran *et al*., 2008). There are some properties of a molecule that can be obtained more easily computationally than by experimental means. Other times, it is used to supplement experimental studies by providing data which are hard to probe experimentally (for example, transition state structures and energies). Thus, many experimental chemists now use computational modelling to gain additional understanding of the compounds being examined in the laboratory. As computational chemistry has become easier to use, professional computational chemists have shifted their attention to more difficult modelling problems (Young, 2001). The types of predictions possible for molecules and reactions include: heats of formation, bond and reaction energies, molecular energies and structures (thermochemical stability), energies and structures of transition states (activation energies), reaction pathways, kinetics and mechanisms, charge distribution in molecules (reactive sites), substituent effects, electron affinities and ionisation potentials, vibrational frequencies (IR and Raman spectra), electronic transitions (UV/Visible spectra), magnetic shielding effects (NMR spectra), geometry optimization from an empirical input, molecular orbitals, dipole (multipole) moments, atomic charges and electrostatic potential, Circular Dichroism (CD) spectra, polarisabilities and hyper-polarisabilities, modelling of excited states and modelling of surface properties (Ramachadran *et al*., 2008). Therefore, computational chemistry can assist the experimental chemist or it can challenge the experimental chemist to find entirely new chemical compounds.

2.3.1 Molecular modeling

Molecular modelling, a subset of computational chemistry, concentrates on describing and predicting the behaviour of individual molecules within a chemical system and their interactions with other molecules in simple mathematical or completely non-mathematical terms. They are very useful because they allow us to predict and understand phenomena without the work of performing the complex mathematical manipulations dictated by a rigorous theory. There are two broad categories of mathematics (Young, 2001):

1. Those that calculate the behavior of the nuclei of the atoms and neglect the behavior of electrons. These are known as molecular mechanics/molecular dynamics (MM/MD) calculations.
2. Those that calculate the behavior of electrons and neglect the behavior of nuclei. These are known as electronic structure calculations.

The most accurate molecular models use ab-initio (first principles) electronic structure methods based upon the principles of quantum mechanics, and are generally very computer intensive. However, due to advances in computer storage capacity and processor performance, molecular modelling has been a rapidly evolving and expanding field, to the point that it is now possible to solve relevant problems in an acceptable amount of time (Davidson and Feller, 1986, 1990; Gece, 2008). However, very few aspects of chemistry can be computed exactly, but almost every aspect of chemistry has been described in a qualitative or approximate quantitative computational scheme (Young, 2001).

All these methods use approximations to simplify the calculations. Although computer software and hardware are improving, and ability to describe chemical structure and behavior is improving, some simplifications to these models must still be accepted. In electronic structure calculations, there are three primary approximations (Young, 2001):

a. The Born-Oppenheimer approximation which states that the motion of the nuclei in molecules can be ignored.

b. The Hartree-Fock (HF) approximation which states that calculations can be simplified by aggregating, or combining the motion of electrons.

c. The Linear Combination of Atomic Orbitals (LCAO) which states that molecular orbitals can be constructed by a relatively straightforward addition of calculated atomic orbitals.

These approximations serve to give us more or less a perfect solution to whatever calculation that is been done.

In the real modelling procedure of a system, the natural criteria associated with the formation of that system should be considered and these factors are incorporated to make the model close to the natural system. All natural processes are associated with at least one of the following criteria (Ramachadran *et al.*, 2008):

i. An increase in stability*:* Stability is a very broad term comprising structural stability, energy stability, potential stability, and so on. During modelling, the thermodynamic (energetic) significance of stability, is to make the energy of the system as low as possible.

ii. Symmetry*:* Nature likes symmetry and dislikes identity. To be more precise, we can say that in nature, no two materials are identical, but they may be symmetrical.

iii. Quantisation: This term stands for fixation. For a stable system, everything is quantised. Properties, qualities, quantities, influences are quantised.

iv. Homogeneity: A number of natural processes such as diffusion and dissolution are associated with the reallocation of particles in a homogeneous manner.

The qualitative and quantitative analysis of molecules on the basis of these criteria is the main objective of computational chemistry and molecular modelling.

2.3.2 Computational Chemistry Methods

There are two main branches of computational chemistry: one is based on **classical mechanics**, and the other is based on **quantum mechanics**. Molecules are sufficiently small objects that, the laws of quantum mechanics must be used to describe them or to predict their structures and properties. However, under the right conditions, it is still sometimes useful (and much faster computationally) to approximate the molecule using classical mechanics. This approach is sometimes called the Molecular Mechanics (MM) or force-field method (Smith *et al.*, 1997). All molecular mechanics methods are empirical in the sense that the parameters in the model are obtained by fitting to known experimental data. Here, the motions of the nuclei are studied and the electrons are not explicitly treated (Born-Oppenheimer approximation). Molecules are seen as a mechanical assemblies made up of simple elements like balls (atoms), sticks (bonds) and flexible joints (bond angles and torsion angles). It treats molecules as a collection of particles held together by simple harmonic forces. These harmonic forces are described in terms of individual potential functions. The overall molecular potential energy or steric energy of the molecule is the sum of the potential functions of its constituents (Young, 2001).

Quantum mechanical methods can usually be classified either as ab-initio or semi-empirical. The first label, ab initio, means from the "beginning" and implies an approach which contains no empirical parameters. This category includes Hartree-Fock (HF), Configuration Interaction (CI), Many-Body Perturbation Theory (MBPT) and Coupled-Cluster (CC) theory. The second category, semi-empirical, includes methods which make serious approximations to the quantum mechanical laws and then employ a few empirical parameters to describe molecules. They are very important in computational chemistry for treating large molecules where the full Hartree-Fock method without the approximations is too expensive. These methods include the modified neglect of differential overlap (MNDO), Austin Model 1 (AM1), and many others. The use of empirical parameters allows some inclusion of electron correlation effects into the methods. It represents a “middle road” between the mostly qualitative results available from molecular mechanics and the computationally time consuming qualitative results available from ab-initio method (Gece, 2008; Ramachandran *et al.*, 2008; Snor, 2009).

2.3.2.1 Density Functional Theory Method

Density functional theory (DFT) methods are quantum mechanical approaches which are hard to categorize as **ab-initio or semi-empirical**. Some DFT methods are free from empirical parameters, while others rely heavily on calibration with experiment. One of the postulates of quantum mechanics is that the wave function contains all information which is known or can be known about a molecule. Hence, quantum mechanical methods provide all possible information about a system, in principle at least. In practice, theoretical chemists have to figure out how to extract the property from the wave function, and then they have to write computer programs to perform the analysis.

However, the underlying principle of density functional theory (DFT) is that the total energy of the system is a unique function of the electron density rather than the wavefunction (Young, 2001; Ramanchandran *et al*., 2008). That is, the energy of the system is written in terms of electron probability density, ρ. For a system of n-electrons, $\rho(r)$ denotes the electron density at a particular point r in space. The electronic energy of the system, E, is said to be a function of the electron density and is denoted $E[\rho]$, in the sense that for a given function $\rho(r)$, there is a single corresponding energy. Hence, it is natural that there exist a large number of computer programs that are designed for calculations of the total energy and its derivatives such as atomic forces and the stress tensor because energy and related properties, including the force constants that define the lattice dynamics of a crystal, are the ground-state properties and hence, the natural products of a DFT calculation. These tools have become valuable in the field of computational crystallography since they allow the application of quantum mechanics for structure prediction, study of chemical bonding, mechanical properties, and lattice dynamics (Gece, 2008; Milman *et al*., 2010).

In this type of calculation, there is an approximate Hamiltonian and an approximate expression for the total electron density. Here, the exact ground state energy of an n-electron system is given by the Kohn-Sham equations:

$$E[\rho] = -\frac{\hbar}{2m_e}\sum_{i=1}^{n}\Psi_i^n(r_1)\nabla_1^2\Psi_i(r_i)dr_i - j_0\sum_{j=1}^{N}\frac{z_i}{r_{i1}}\rho(r_1)dr_1 + \frac{1}{2}j_0\int\frac{\rho(r_1)\rho(r_2)}{r_{12}}dr_1dr_2 + E_{XC}[\rho] \qquad 2.58$$

where the one-electron spatial orbitals, Ψ_i(i = 1, 2… n) are the Kohn-Sham orbitals, and the exact ground state electron density is given by:

$$\rho(r) = -\sum_{i=1}^{n}|\Psi_i(r)|^2 \qquad 2.59$$

The sum is over all the occupied Kohn-Sham (KS) orbitals; ρ is known once these orbitals are computed. The first term on the right in equation (2.58) represents the kinetic energy of the electrons; the second term represents the electron-nucleus attraction where sum is over all N nuclei with index I and atomic number Z_1; the third term represents the Coulomb interaction between the total charge distribution (summed over all Kohn-Sham orbitals) at r_1 and r_2; the last term is the exchange-correlation energy of the system which is also a functional of the electron density and takes into account all the effects due to electron spin. The KS orbitals are found by solving the KS equations, which are derived by applying the variational principle to the electronic energy $E[\rho]$ with the charge density given by equation *2.59* above.

There are roughly three categories of density functional methods. The simplest approximation is the **Local-Density Approximation** (LDA) methods which assume that the density of the molecule is uniform throughout the molecule. **Gradient-Corrected** (GC) methods account for the non-uniformity of the electron density while **Hybrid** methods incorporate some of the more useful features from ab-initio methods (Hartree-Fock methods) with improvement of DFT mathematics.

Generally, DFT is used to investigate the electronic structure, principally the ground state of many-body systems, in particular atoms, molecules and the condensed phases. The main objective of is to replace the many-body electronic wave function with the electronic density as the basic quantity, combining the exchange functional with the correlation functional in its calculations. For example, the notation B3LYP/6-31G* denotes a density functional calculation done with the Becke's 3-parameterised hybrid exchange functional and the Lee-Yang-Parr correlation functional, with the orbitals expanded in a 6-31G* basis set. Computational demands with DFT methods are much less than with ab-initio methods of similar quality. Hence, DFT methods are widely used in computing larger molecules such as organic, bio- and inorganic molecules (Micheal, 2002; Ramachandran *et al*., 2008; Milman *et al*., 2010). The extension of DFT is the **Time-Dependent Density Functional Theory** (TD-DFT). Their conceptual and computational foundations are analogous to show that the (time-dependent) wave function is equivalent to the (time-dependent) electronic density, and then to derive the effective potential of a fictitious non-interacting system which returns the same density as any given interacting system. The issue of constructing such a system is more complex for TD-DFT, most notably because the time-dependent effective potential at any given instant depends on value of the density at all previous times. But, it is the popular density functional based approach to excitation energies (Ramachandran *et al*., 2008).

2.3.3 Basis Sets

Basis sets are series of mathematical functions used by computational chemistry software to begin the process of describing where the electrons are in proximity to the nucleus and to each other. In quantum chemical calculations, the term basis set is applied to a collection of contracted Gaussians representing atomic orbitals, which are optimised to reproduce the desired chemical properties of a system. Standard ab-initio software packages generally provide a choice of basis sets that vary both in size and in their description of the electrons in different atomic orbitals. Larger basis sets include more and a greater range of basis functions. Therefore, larger basis sets can better refine the approximation to the true molecular wavefunction, but require correspondingly more computer resources. Alternatively, accurate wavefunctions may be obtained from different treatments of electrons in atoms. For instance, molecules containing large atoms ($Z > 30$) are often modelled using basis sets incorporating approximate treatments of inner-shell electrons which account for relativistic phenomena (Davidson and Feller, 1986).

The minimum number of Atomic Orbital (AO) basis functions needed to describe each electron in an atom is **minimal basis sets** (*e.g.*, 1s for H and He; 1s, 2s, $2p_x$, $2p_y$, $2p_z$ for Li to Ne). An example of a minimal basis set is STO-3G, which uses three Gaussian-type functions (3G) per basis function to approximate the atomic Slater-type orbitals. Although minimal basis sets are not recommended for consistent and accurate predictions of molecular energies, their simple structure provides a good tool for visualising qualitative aspects of chemical bonding. There are two shortcomings with using a minimal basis set for molecular systems. All the basis functions are either spherical (as in s functions) or come in sets that describe a sphere (as in p function), indicating that only atoms with spherical environment are better described by minimal basis sets (Micheal, 2002). The other shortcoming of a minimal basis sets is that basis functions which are atom centered. This restricts the flexibility of the functions to describe electron distribution between the nuclei to form chemical bonds, and makes molecule too ionic and bonds too long (Micheal, 2002).

The first shortcoming of minimal basis sets can be resolved by introducing **split valence** basis sets which add more functions (one contracted Gaussian plus some primitive Gaussians) to the basis sets. In these basis sets, the valence atomic orbitals are split into two parts: an inner compact orbital, and an outer diffuse one. It takes into account that valence electrons are the electrons that are involved in bonding and chemical reactions, as opposed to core electrons, which are not involved in reactions. '**Double zeta**' basis sets use two basis functions to describe valence electrons, 'triple zeta' use three functions, and so forth. Basis sets developed by Pople and co-workers are denoted by the number of Gaussian functions used to describe inner and outer shell electrons. Thus '6-21G' describes an inner shell atomic orbital with a contracted Gaussian composed of six primitive Gaussians, an inner valence shell with a contracted Gaussian composed of two primitives, and an outer valence shell with one primitive. Other split-valence sets include 3-21G, 4-31G, and 6-311G (Davidson and Feller, 1986).

The second shortcoming was addressed by adding **polarisation** functions to basis sets (i.e polarization basis sets) to allow for non-uniform displacement of charge away from atomic nuclei, thereby improving descriptions of chemical bonding. Polarisation functions describe orbitals of higher angular momentum quantum number than those required for the isolated atom (*e.g.*, *p*-type functions for H and He, and *d*-type functions for atoms with $Z > 2$), and are added to the valence electron shells. For example, the 6-31G (d) basis set is constructed by adding six *d*-type Gaussian primitives to the 6-31G description of each non-hydrogen atom. The 6-31G (d, p) is identical to 6-31G (d) for heavy atoms, but adds a set of Gaussian *p*-type functions to hydrogen and helium atoms. The addition of *p*-orbitals to hydrogen is particularly important in systems where hydrogen is a bridging atom (Micheal, 2002).

Species with significant electron density far removed from the nuclear centres (*e.g.*, anions, lone pairs and excited states) require **diffuse functions** to account for the outermost weakly bound electrons. Diffuse basis sets are recommended for calculations of electron affinities, proton affinities, inversion barriers and bond angles in anions. The addition of diffuse *s*- and *p*-type Gaussian functions to non-hydrogen atoms is denoted by a plus sign as in '3-21+G'. Further addition of diffuse functions to both hydrogen and larger atoms is indicated by a double plus (Micheal, 2002).

2.3.4 Quantum Chemical Parameters

Quantum chemically derived parameters enable the definition of a large number of molecular quantities characterising the reactivity, shape, and binding properties of a complete molecule as well as of molecular fragments and substituents. The use of theoretical parameters presents two main advantages: firstly, the compounds and their various fragments and substituents can be directly characterised on the basis of their molecular structure only; and secondly, the proposed mechanism of action can be directly accounted for in terms of the chemical reactivity of the compounds under study. These parameters are fundamentally different from experimentally measured quantities, although there are some natural overlaps. Unlike experimental measurements there is no statistical error in quantum chemical calculations. There is inherent error however, associated with the assumptions required to facilitate the calculations. In most cases, the direction but not the magnitude of the error is known. In using quantum chemistry-based parameters with a series of related compounds, the computational error is considered to be approximately constant throughout the series (Gece, 2008). The quantum chemical parameters considered in this thesis are as follows:

2.3.4.1 Molecular orbital energies and associated properties

Highest occupied molecular orbital energy (E_{HOMO}) and lowest unoccupied molecular orbital energy (E_{LUMO}) are very popular quantum chemical parameters. These orbitals, also called the frontier orbitals, determine the way the molecule interacts with other species. The HOMO is the orbital that could act as an electron donor, since it is the outermost (highest energy) orbital containing electrons. The LUMO is the orbital that could act as the electron acceptor, since it is the innermost (lowest energy) orbital that has room to accept electrons. According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between the frontier orbitals (HOMO and LUMO) of reactants. The energy of the HOMO is directly related to the ionisation potential and the energy of the LUMO is directly related to the electron affinity. The LUMO ‑ HOMO gap, i.e. the difference in energy between the HOMO and LUMO, is an important stability index (Bo *et al*., 2011). A large LUMO - HOMO gap implies high stability (kinetic stability) for the molecule interacting. The concept of ‘activation hardness’ has been also defined on the basis of the LUMO - HOMO energy gap. The qualitative definition of hardness is closely related to molecular polarisabilities, since a decrease of the energy gap usually leads to easier polarisation of the molecule. Furthermore, this explains the eventual charge transfer interactions taking place within a molecule as a result of the ease of electron distribution (Gece, 2008; Kavitha *et al*., 2010; Sridevi *et al*., 2012 and Praveen *et al*., 2012). Thus, the global hardness (η) is associated with the stability and reactivity of a chemical system, while the Electron Affinity (EA) can be used in combination with Ionization Energy (IE) to give electronic chemical potential (χ), a measure of the escaping tendency of electrons from equilibrium. For an N-electron system with total electronic energy (E) and an external potential $v(\vec{r})$; χ known as the negative of electronegativity (χ) has also been defined as the first derivative of the (E) with respect to N at $v(\bar{r})$. Global hardness has been defined within the DFT as the second derivative of the E with respect to N (Gerlings *et al.*, 2003; Shubin, 2005).

The ionization energy, the electron affinity, the global electrophilicity (ϖ) which measures the stabilization in energy when the system acquires an additional electronic charge from the environment and global softness (S) are also indicators of high succeptibility or unstability of molecules to UV-spectroscopy (i.e its high reactivity). These are as expressed below:

$$\varsigma \approx \frac{-(I+EA)}{2} \approx {}^{1}\!/_{2}\,(E_{HOMO} + E_{LUMO}) \qquad 2.60$$

$$\eta \approx \frac{IE-EA}{2} \approx {}^{1}\!/_{2}\,(E_{LUMO} - E_{HOMO}) \qquad 2.61$$

$$\varpi \approx {}^{\varsigma^{2}}\!/_{2\eta} \qquad 2.62$$

$$EA \approx -E_{LUMO} \qquad 2.63$$

$$S \approx {}^{1}\!/_{2\eta} \qquad 2.64$$

$$IE \approx -E_{HOMO} \qquad 2.65$$

$$\chi \approx \frac{\mathrm{I+EA}}{2} \qquad 2.6$$

2.3.4.2 Dipole moment (*μ*)

The most widely used quantity to describe the polarity of a system is its dipole moment. It is the measure of polarity of a polar covalent bond and is defined as the product of charge on the atoms and the distance between the two bonded atoms. The total dipole moment, however, reflects only the global polarity of a molecule. For a complete molecule the total molecular dipole moment may be approximated as the vector sum of individual bond dipole moments. The dipole moment in a molecule is an important property that is mainly used to study the intermolecular interactions involving the non-bonded type dipole-dipole interactions, because the higher the dipole moment, the stronger will be the intermolecular interactions. It has also been reported that the dipole moments of molecular systems increases with a decrease in the LUMO - HOMO energy gap (Atkins and de Paula, 2006; Gece, 2008; Praveen *et al.*, 2012; Sridevi *et al.*, 2012).

2.3.4.3 Polarisability (α)

This is the measure of the distortion of a molecule in an electric field, as applied electric field can distort a molecule as well as align its permanent electric dipole moments. Thus, in an electric field of strength ξ, the induced dipole moment μ of a molecule would be directly proportional to the electric field strength. This is expressed as:

$$\mu = \alpha \xi \qquad 2.67$$

where the constant of proportionality (α) is the polarisability of the molecule. The larger the polarisability, the larger the induce dipole moment of a molecule for a given applied field. Hence, polarisability is often expressed as a volume quantity known as polarisability volume, α':

$$\alpha' = \frac{\alpha}{4\pi\varepsilon_0} \qquad 2.68$$

For molecules that are polarisable, when the applied electric field increases by dξ, the energy of the molecule would change by $-\mu^* d\xi$. As such, the change in energy of the molecule when the field is increased from 0 → ξ would be:

$$\Delta E = -\int_0^{\xi} \mu^* d\xi \qquad 2.69$$

Comparing equation (*2.67)* and (*2.69*),

$$\Delta E = -\int_0^{\xi} \alpha\xi d\xi \quad = -\frac{1}{2}\,\alpha\,\xi^2 \qquad 2.70$$

The contribution of the Hamiltonian when a dipole moment is exposed to an electric field is:

$$H^{'} = -\mu\xi \qquad 2.71$$

By comparing equations (2.70) and (2.71), it is obvious that the second-order perturbation theory is invoked in the calculation of the energy of such system in the presence of an electric field. This is the only way an expression proportional to ξ^2 would be obtained. According to this theory, the second-order contribution to the energy of the system is given by:

$$E^{(2)} = \sum_n \frac{\left|\int \Psi_n^* \; H^{'} \; \Psi_0 d\tau\right|^2}{E_n^{(0)} - E_0^{(0)}} \qquad 2.72$$

But because the wavefunction is normalised, this is reduced to:

$$E^{(2)} = \sum_n \frac{|H^{'}|^2}{E_n^{(0)} - E_0^{(0)}} = \sum_n \frac{|\mu\xi|^2}{E_n^{(0)} - E_0^{(0)}} = \xi^2 \sum_n \frac{|\mu_{0n}|^2}{E_n^{(0)} - E_0^{(0)}} \qquad 2.73$$

where μ_{0n} is the transition dipole moment and can be in any direction. The prime indicates that states with *n* as zero are omitted. When equations (*2.73*) and (*2.70*) are compared, the expression in *2.74* is obtained:

$$\alpha = 2\sum_n \frac{|\mu_{0n}|^2}{E_n^{(0)} - E_0^{(0)}} \qquad 2.74$$

Because μ = q d where *q* is the charge on the system and *d* is the distance separating the charges on the system (molecular radius), and $E_n^{(0)} - E_0^{(0)}$ can be approximated to the energy difference between the energies of the frontier molecular orbitals (E_{LUMO} E_{HOMO}) gap denoted as Δ*E*, equation (*2.74*) becomes:

$$\alpha = \frac{2(qd)^2}{\Delta E} \qquad 2.75$$

This shows that the polarisability of a molecule increases with the size of the molecule and a decrease in the energy difference between the frontier molecular orbitals. This property enables the determination of the strength of molecular interactions (e.g. long-range intermolecular induction, dispersion forces) as well as the cross sections of different scattering and collision processes, and optical properties of a system. A molecule with a low frontier orbital gap is more polarisable and is generally associated with a high chemical reactivity, low kinetic stability and is termed as soft molecule (Atkins and de Paula, 2006; Sundaraganesan *et al*., 2009 and Sridevi *et al*., 2012)

2.4. Review of literature on the compounds being studied

2.4.1 9,10-phenanthrenequinone

Since the first reports of the light catalysed reaction of phenanthrene to 9,10-phenanthrenequinone (Figure 1.1) by Klinger (Binoy, 2000), many other researchers (Jonathan *et al*., 1996, Barbas *et al*., 1996) have reported on its preparation, photocatalysis of its formation from phenanthrene, its inhibiting biodegradation of naphthalene and its photochemical reactions. Johannes and Sally (1988) reported the conversion of benzoin to PQ by photocyclization of its adducts with phenyl boric acid followed by hydrolysis of the photoproduct. Sawaski (1983) and Barbas *et al*., (1996) reported the photochemical oxidation and photoepoxidation of PQ to the ring opened dicarboxylic acid products while Arfesten *et al*., (1996) reported the increased toxicity of its oxidation products to eukaryotes. Shimberg (1958) has also described the studies of photochemical addition reaction of phenanthrenequinone and related O-quinones. These include the addition of sulphur (IV) oxide (SO_2) to form a cyclic sulphate. Chow *et al*., (1970) studied the photo oxidation of α-diketones to olefins and its photo reduction by hydrogen or electron donors (alcohol, hydrocarbons, ethers) that are in turn oxidized. This indicates that PQ may also interact with varieties of biomolecules. The report that describes the photochemical addition of ethers to PQ represents the example of what promises to be a general class of a suspension of phenanthrenequinone in dioxane Chow *et al*., (1970). The phosphorescence and Luminescence properties of phenanthrenequinone in different solvents as described by Kuboyama and Sanae (1969) indicated that, in the luminescence, there was apparent washing out as the chain length of the solvent increased, which is ascribed to a decrease in the intensity of the absorption lines.

The bands and lines position are due to different types of centers than due to the transitions involving or not involving phosphorescence at the same types of centres. The phosphorescence bands lifetime and excitation spectra studied at 77^{o}K in rigid solution and in crystal state show that in a rigid solution, the life time of these phosphorescence bands are in the range of 10-0.1 m sec. And, the solvent effect on the lifetimes show clear differences between ortho and para quinones. This is similar to n-π* bands of these compounds .The para quinones are identified with n-π* bands and in crystal states, it is at longer wavelength than in rigid solution while the lifetimes of the former are far longer than those of the latter (Kuboyama *et al*., 1975). The characterization of the excited state of PQ and its derivatives substituted in the position 3 and 6 with methoxy, chloro, methyl, fluoro groups was carried out using steady ultraviolet absorption spectroscopy and phosphorescence emission spectroscopy at room temperature and 77k by Barbas *et al*., (1996). It was observed that the derivatives show slightly higher triplet energy than phenanthrenequinone and that the singlet and triplet energies increases with electron donating groups.

The relative rate of hydrogen abstraction of the triplet state of PQ studied by Kazuhiro *et al*., (1969) indicated the great ability of hydrogen abstraction of photo activated PQ from hydrogen donor. This reflection shows that PQ can be reduced easily when it is irradiated in benzene. It was also reported that it has maximum absorbance at 410-420mμ which may correspond to n-π* absorption band because it can be reduced even if it is irradiated with visible light.

2.4.2 2,3-diphenylcyclopropenone

This compound was first synthesized by Breslow and Vol' pin from cycloaddition reaction product of carbene to ketene acetal in 1959 (Brestlow *et al.*, 1965). Since then, several publications have appeared describing the properties and reactions of this interesting substance. It was claimed that except 2,3-diphenylcyclopropenone **(**Figure 1.1**)**, no stable compound is known to contain a carbonyl group in three member rings (Billips and Moorehead, 1987) and this has been known to affect its aromaticity when compared with tropone. This allowed the preparation of many acid-base complexes of cyclopropenone with many acids (Potts and Baum, 1974; Chicheester 1987). Also, it was claimed by Hanton and Banwell (1987), as well as, Billips and Moorhead (1987) that the carbonyl oxygen of DPCP is more basic than those of most ketone as a consequence of the comparatively high polarization of CO group.

Moreover, the stability of DPCP, as reported earlier by Breslow *et al.*, (1965) is not from the attached phenyl ring or groups but a properties of 3-atoms, 2-electron grouping, as diphenylcyclopropenium has a peculiar interaction properties of close analogy with tropone, This is suggesting a partial expulsion of an electron unto the carbonyl oxygen, leaving an aromatic sextet in the seven membered ring (Coffey, 1962). Infra-red spectra study of the compound in carbon tetrachloride (CCl_4) was done by Brestlow in 1959 to propose the structure of the compound. The Infra-red spectrum in CCl_4 shows weak absorption at 3.4 μ (aromatic C-H), a strong band at 5.4 μ (C= O stretching) and rather strong bands at 6.0μ (conjugated C=C stretching), 6.7 μ and 6.9 μ (benzene ring) and 7.45 μ (C=O bending). The only other major absorption bands are in carbondisulphide (CS_2) at 13.0 μ and 14.5 μ in monosubstituted benzene.

A good evidence for strong polarization DPCP is its dipole moment which was found to be 5.14D (Chin *et al.*, 2007; Kazimanich *et al.*, 2008) but comparison of either value with 3.0D for benzophenone, the 4.0D for tropone and 5.03D for trimethylamine oxide indicated that diphenyl cyclopropenone is indeed very strongly polarized. This is also reflected in the high basicity of DPCP and its other derivatives (Chin *et al.*, 2007).

2.4.3 Thiophene and its derivatives

Meyer (1883) established the formular of thiophene to be C_4H_4S. It was prepared by the reaction of 1, 4-diketone and H_2S in the presence of anhydrous HCl at 0-40^oC (Magaret, 1949). Substitutions on the thiophene ring are reported to affect the spectrum in a way which depends on the type and position of the substitution. Ostman (1969) used (omega) ω–technique and p- and d-orbital model for the π-orbital and showed that α position in the thiophene is more active than β position while Sugomoto *et al*., (1959) related the position of longest wavelength band of 2-substituted thiophene to the band of mono-substituted benzene.

The electronic structures of 3,4-diphenylthiophene (Figure 1.1) are of great interest, since erylthiophene are of chemical and biological importance, yet their chemistry has made no remarkable progress as reported by Abu Ettitah and Hillal in 1959. These workers reported that the band maximum observed in the 3,4-diphenylthiophene(DPT) are due to π–π* transition since their value remain unchanged in both polar and non-polar solvent and that the charged transfer character is not apparent in the observed transitions. The value of the oscillator strength reported in methanol at 255nm and 230nm are 0.13 and 0.34 respectively for DPT. It was also confirmed that DPT exhibits significant steric inhidrance and that the spectra of this composite molecule is the additive spectra of the sub-system (Abu Ettitah and Hillal, 1959).

Moreover, the photo physical, crystallographic and electrochemical characterization of symmetric and unsymmetric self-assembled conjugated thiopheno azomethines was studied by Sergio *et al*., (2007). The fluorescence and phosphorescence of the thiopheno azomethines measured are found to be similar to those of thiophene analogous that had previously being used in functional devices. The dynamic and stoichiometric of thiophene adsorption and of rearrangement of thiophene–derived adsorption specie in O, He, H carrier using chromatographic method and mass spectroscopic on H-ZSM5 and H-Y zeolites studied by Antonio and Karl (2004) show that adsorption was found to obey Langmuir isotherms on both zeolites which shows that the adsorption of thiophene is selectively greater than expected due to Van-der Waals interactions (Jackson, 1987).

2.4.4 Furan and its derivatives

Several methods had been reported for the synthesis of furan (an unsaturated analogous of tetrahydrofuran), its many derivatives and synthones by many researchers and authors (Coufolini and Dong, 1996; Hassan and Monirah, 2010). Vibrational analysis of furan has also been extensively studied by Busser (1955), Bak *et al*., (1955) on the Infra-red spectra and by Daasch (1954) on the Raman spectra. Structural parameters of furan have been obtained by electron diffraction methods (Schomaker and Pauline, 1939) while its extensive microwave studies were reported by Bak *et al*., in 1955. These investigators showed that furan molecule has planar structure and that this five member ring molecule is almost, but not quite a regular pentagon. Hence, the molecule is slightly asymmetric with C_{2v} symmetry. This is reported to have been indicated by broadening of the spectra lines (Schomaker and Pauline, 1939).

The nuclear magnetic spectra of the ring protons were reported to have τ-value very much shifted downfield compare with the corresponding aromatic compound which is even more pronounced for hydrogen atoms at the β-positions. This is attested to be due to inductive effect of the hetero atom at this position (Finar, 1982).The rotational Raman spectra of furan and cyclopentene as reported by Benedicts and Alfons (1965) show reliable values for the ground state rotational constant from electron diffraction and microwave investigation. There are no reports on the values of centrifugal distortion constants of furan but the microwave value of carbon distortion constant of cyclopentene differs by large amounts from the values that are expected for cyclic molecules. The dipole moment of furan and furan-argon were determined as 0.685D and 0.701D respectively from stark shifts by the use of a cavity Fourier Transform Microwave (FTMW) spectrometer (Jung-Jing *et al*., 1990). The larger moment of the complex, being in contrast to isoelectronic pyrrole and pyrrole-argon, where a decrease was observed from 1.767D to 1.707D. The changes were attributed to induced dipole moment in the argon. Ab-initio calculation of the electric field at the argon site were also used to estimate the induced dipole component for comparison with the experimental values and the reports show that this agrees much better than the estimates obtained by employing the dipole and quadruple moments of the heterocycles (Jung-Jing *et al*., 1990).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Spectroscopic measurement

3.1.1 Solvents

The solvents used were n-heptane, cyclohexane, ethanol, methanol, dichloromethane, 1,2-dichloroethane, tetrahydrofuran and acetonitrile. These were products of British drug House Limited (BDH) which were redistilled twice before used. Their boiling points were used as index of purity.

3.1.2 Compounds

The compounds studied were 9,10-phenanthrenequinone (PQ); furan-3,4-dicarboxylic acid (DCF); 3,4-diphenylthiophene(DPT); 3,4-dicarboxylic-2,5-diphenylthiophene (DCDPT); benzo[b]thiophene and 3-diphenylcyclopropenone(DPCP). These were spectroscopic grade products of Aldrich Chemicals which were used without further purification. Their molecular structures, molecular formula, Molecular Mass (MM) and abbreviations are as presented in Figure 1.1.

3.1.3 Ultraviolet-visible spectra measurement

Diluted solutions of the compounds studied were prepared in 5mls standard flasks in the concentration range of 10^{-6} M - 10^{-4} M. Their spectral analyses were carried out using Shimadzu *UV-1650* double beam spectrophotometer coupled with UV-probed 2.31 version (software) and operated in the wavenumber range (25,000 - 52,631) cm^{-1}. A pair of matched quartz cuvettes, each of 1cm pathlength was used, one of which contained the sample solution and the other, the pure reference solvent which served as a blank or baseline for the solutions absorption bands. The sample compartment was thermostated at $25^{o}C$. The spectra were recorded with the instrumental band set at 0.2 - 1.0 nm and ran with the scan speed of 2 nm per second. The spectra scan process was done to obtain the absorption spectra of the compounds. This process was repeated for all the compounds in different solvent. Under this condition, it was observed that 0.02 absorbance, corresponding to a 20 cm graphical full scale recording yielded spectra of satisfactory sensitivity and resolution.

Absorbance for each band was converted to molar absorptivities. The plots of molar extinction coefficient against wave number as shown in Figures 4.1-4.8 were used to determine the transition energies of the bands. The oscillator strength (f) in solution from states i to j $f_{aij\,(s)}$ were calculated using the equation *2.55* (Iweibo *et al*., 1990).

3.1.4 Calculation

3.1.4.1 Concentration of stock solution of the solute.

The concentration of the standard solute C_s prepared was calculated using the expression below:

$$C_s = \frac{m}{M_m} \times \frac{1000}{V}\ mol\ dm^{-3} \qquad 3.1$$

where $m(g)$ is the mass of the solute, M_m $(gmol^{-1})$ is the Molecular Mass (MM) of the solute and V(cm^3) is the volume of the volumetric flask.

3.1.4.2 Calculation of the concentration of solute used for analysis.

The concentrations C_s' of solute used for analysis were determined using equation 3.2, where V_s is the volume of the stock solution pipetted into 2cm^3 blank solvent and the volume of the solution in the cuvette is $(2 + V_s)$

$$C_s'\,(2 + V_s) = C_s\ \ V_s \qquad 3.2$$

3.1.5 Data Analysis

3.1.5.1 Computation of Oscillator Strength.

The experimental oscillator strength in solution $f_{aio(s)}$ for each absorption band in the spectra of the molecules studied were calculated as a measure of the intensity of absorption of the molecules by means of equation *2.55* which addresses both the solvent and field correction factor for the oscillator strength. The integral $\varepsilon_{(\bar{v})}d\bar{v}$ were calculated using the assumptions of symmetrical bands in conformity with Gaussian distribution as reported by Iweibo (1982). The vapour phase oscillator strength $f_{aio\,(v)}$ values were also computed using the modified Onsager-Abe reaction field model of equation *3.3* which is an equivalent form of equation *2.5*.

$$f_{aio\,(s)} \big/ f_{aio\,(v)} = \phi \qquad 3.3$$

where $\phi = \frac{9n^3}{(2n^2+1)^2}$, the correction factor on changing from solution phase to vapour phase, n is the refractive index of each of the solvent used and $f_{aio\,(v)} \neq 0$

3.1.5.2 Determination of transition dipole moment (Δμ) and transition polarizability (Δα)

Using Clausuis-Mossotti expression (Weast, 1985-1986) of equations 3.*4* and *3.5*, the theoretical ground state electric polarizability (α_g) for the solutes were calculated from the molar refraction (R) of bond atoms for each compound in different solvent in accordance with Schuyer, Blom and Van krevelen (Iweibo, 1991), the Einstein coefficient (k_{ji}) for each solute was calculated using equation *3.6* while the theoretical ground state electric dipole moment (μ_g) of the selected solvent used were computed where necessary from the measurement of stark effect in the microwave spectrtroscopy of gas expression (Weast, 1985-1986).

$$\propto = {}^{3}/_{4\pi N_0}\,(R) \qquad 3.4$$

$$R = \left(\frac{n^2-1}{n^2+2}\right)\frac{M}{d} \qquad 3.5$$

$$k_{jis} = \frac{D^2}{6\,\varepsilon_0\,\hbar^2} = \frac{e^2}{4\,\varepsilon_0\,\mathrm{m_e\,hc}}\left(\frac{f_{aio(s)}}{\bar{\nu}_{max}}\right) \qquad 3.6$$

R is the molar refraction; N_0, the Avogadro's number (mol^{-1}); M being the molecular mass of the molecule under investigation; d, the density (gcm^{-3}) of solvent in which the molecule is dissolved; $\bar{\nu}$, frequency in wave number; ε_0, the vacuum permittivity; D, the transition integral; h, the Planck's constant; $f_{aio\,(s)}$ is the solution phase oscillator strength for each band while $\mathrm{m_e}$ and e are the mass of an electron and charge of a photon respectively. Equations 2.48, 2.49 and 2.50, developed from the intensity perturbation approximation relate the square root of oscillator strength in solution $f_{aio\,(s)}^{\frac{1}{2}}$ to that of the vapour $f_{aio\,(v)}^{\frac{1}{2}}$, to the stark terms $\left(\frac{\mu_{\beta 00}}{r_{\alpha\beta}^3}\right)$, the integral Einstein co-efficient (k_{ij}), ground state electric polarizability of the solute (α_g), transition dipole moment $(\Delta\mu)$ and transition dipole polarizability $(\Delta\alpha)$ as well as, the ratio of the change in the transition energies of the solute to that of the solvent $\left(\frac{\Delta E_{solute}}{\Delta E_{solvent}}\right)$, where $\frac{\alpha_g}{r_{\alpha\beta}^3} = X_1$, $\frac{\mu_{\beta 00}}{r_{\alpha\beta}^3} = X_2$ and $r_{\alpha\beta}$, the inter-nuclear distance between the solute and the solvent molecule. These equations show that many data on the solvent and the solute were required to permit their uses reliably in order to determine the transition dipole moment and transition polarizability of molecules. Some of the data on these parameters are obtainable from standard handbook of Chemistry and Physics while some were computed by means of established procedure (Weast *et al*, 1985-1986).

3.2 Computational studies

Computational studies were initiated by drawing the molecular structures of the compounds investigated with 2D-MODEL program. After the drawing, Arguslab model was employed for their structural optimization. The transition energies, the wavelength of maximum absorption and corresponding oscillator strength for the transitions in UV-region were done with Becke's three-parameter hybrid exchange correlation functional with the Lee, Yang, and Parr's correlation functional from Time-Dependent Density Functional Theory using 6-31G* basis set (i.e. TD-DFT B3LYP/6-31G*) computation by Gaussian' 2003. Other properties calculated for the optimized structures of the studied compounds included the dipole moment, polarizability, transition dipole moment, transition polarizability, HOMO and LUMO energies, the global parameters such as electronegativity, global hardness, global softness, the chemical potential, electrophilicity index and electron affinity. Although, the possibilities of verification of the calculated geometrical structures by the corresponding data are limited, but it has been reported that TD-DFT B3LYP/6-31G* optimization correctly reproduces experimental structures of molecules (Deperasinska, 2007). In the light of this finding, it is believed that geometries of the studied molecules as used were correct.

CHAPTER FOUR

RESULTS

4.1 Experimental Data

4.1.1 UV–visible absorption spectra

The recorded room temperature electronic absorption spectra of the studied compounds depicting the effect of solvents and substituents on their spectral profiles are as shown in Figures 4.1-4.9, where these has been converted from the fixed band wavelength absorption experiment to wave number scales. The spectra band shapes were then decomposed into Gaussian components for effective calculation of the oscillator strength of the observed transition bands in each compound. For each compound, only the spectra in the represetative solvents (methanol, dichloromethane and n-heptane) have been displayed in order to avoid overcrowding of symbols and masking of the salient's spectral features.

4.1.2 Transition energies and Maximum molar absorptivity [$\varepsilon_{(v_{\max})}$]

The detailed characterization of the spectral properties of the studied compounds vis-a vis the transition energies in wavenumber (cm^{-1}), the maximum molar extinction coefficient $\left(M^{-1}cm^{-1}\right)$ of the compounds in ethanol, methanol, tetrahydrofuran, acetonitrile, 1,2-dichloroethane, dichloromethane, n-heptane and cyclohexane are as presented in Table *4.1*.

4.1.3 Oscillator strength in solution and in vapour phase

Table *4.2* summarises the experimentally determined oscillator strength in solution $f_{aio(s)}$ and the calculated vapour phase oscillator strength $f_{aio(v)}$ using modified Onsager-Abe reaction field model.

4.1.4 Transition dipole moments (Δμ) and transition polarizabilities (Δα)

The regression plots of data obtained for the solvent and substituents perturbation of the electronic intensities according to equations 2.49 of section 2.2.4 for the compounds studied are as presented in Figures 4.10-4.14. Tables 4.7-4.9 summarize the transition dipole moment and transition polarizabilities of the different transitions for these compounds as obtained from the analysis of the plots.

4.2 Computational Data

The optimized geometries of DPCP, PQ, DCF, BT, DPT, and DCDPT are as presented in Figures 4.15-4.20. Tables 4.10-4.15 show the computed singlet state excitation energies (eV), wavelengths (cm^{-1}) and oscillator strengths while Tables 4.15-4.17 present the theoretically computed transition dipole moment (D) of the compound and Tables 4.18-4.20 signify the computational data on the quantitative structure properties relationship of the molecules using TD-DFT B3LYP/6-31G* method.

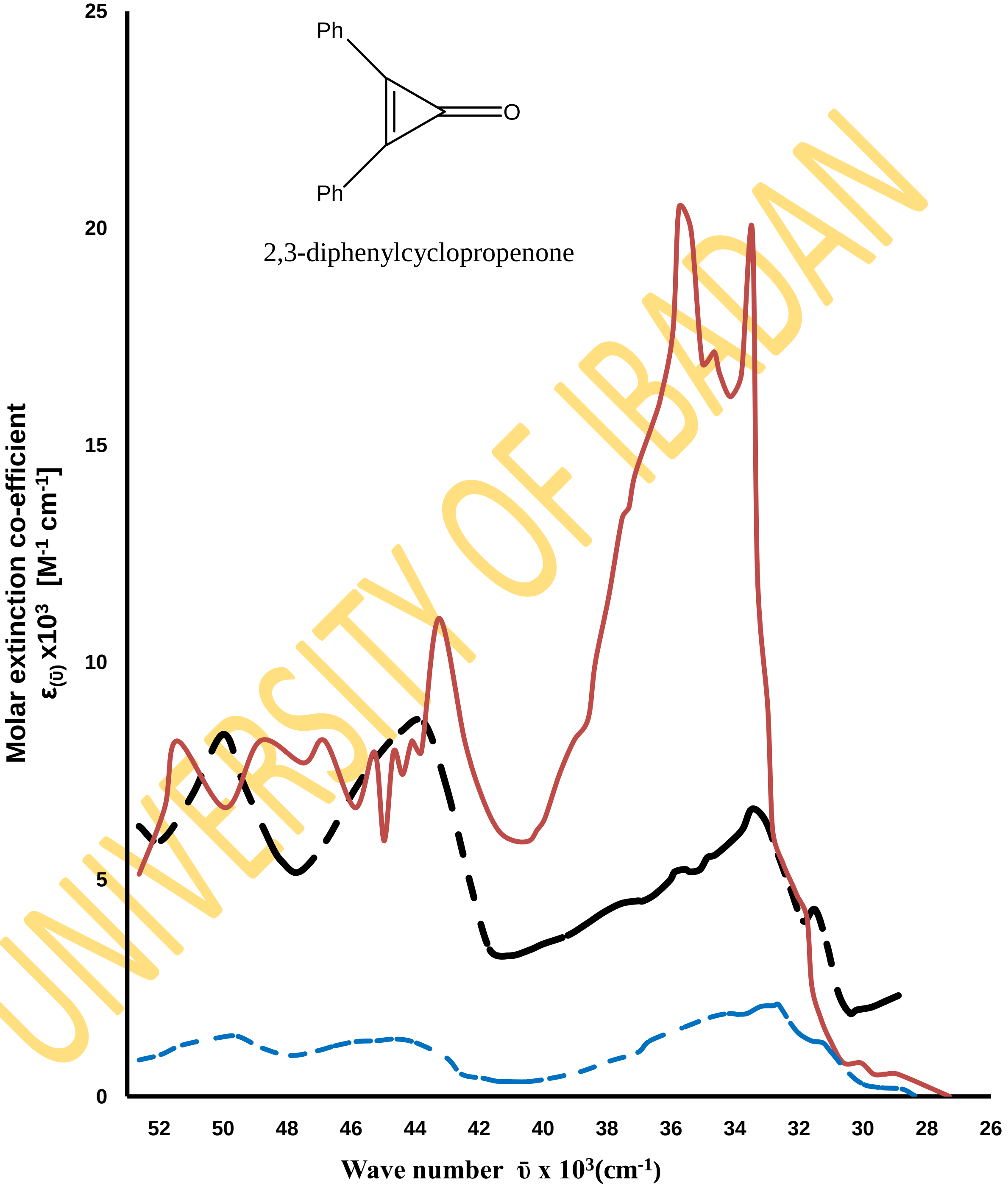


Figure 4.1: **Electronic absorption spectra of 2,3-diphenylcyclopropenone in methanol (-. -. -.),dichloromethane (___) and heptane (- - -)**

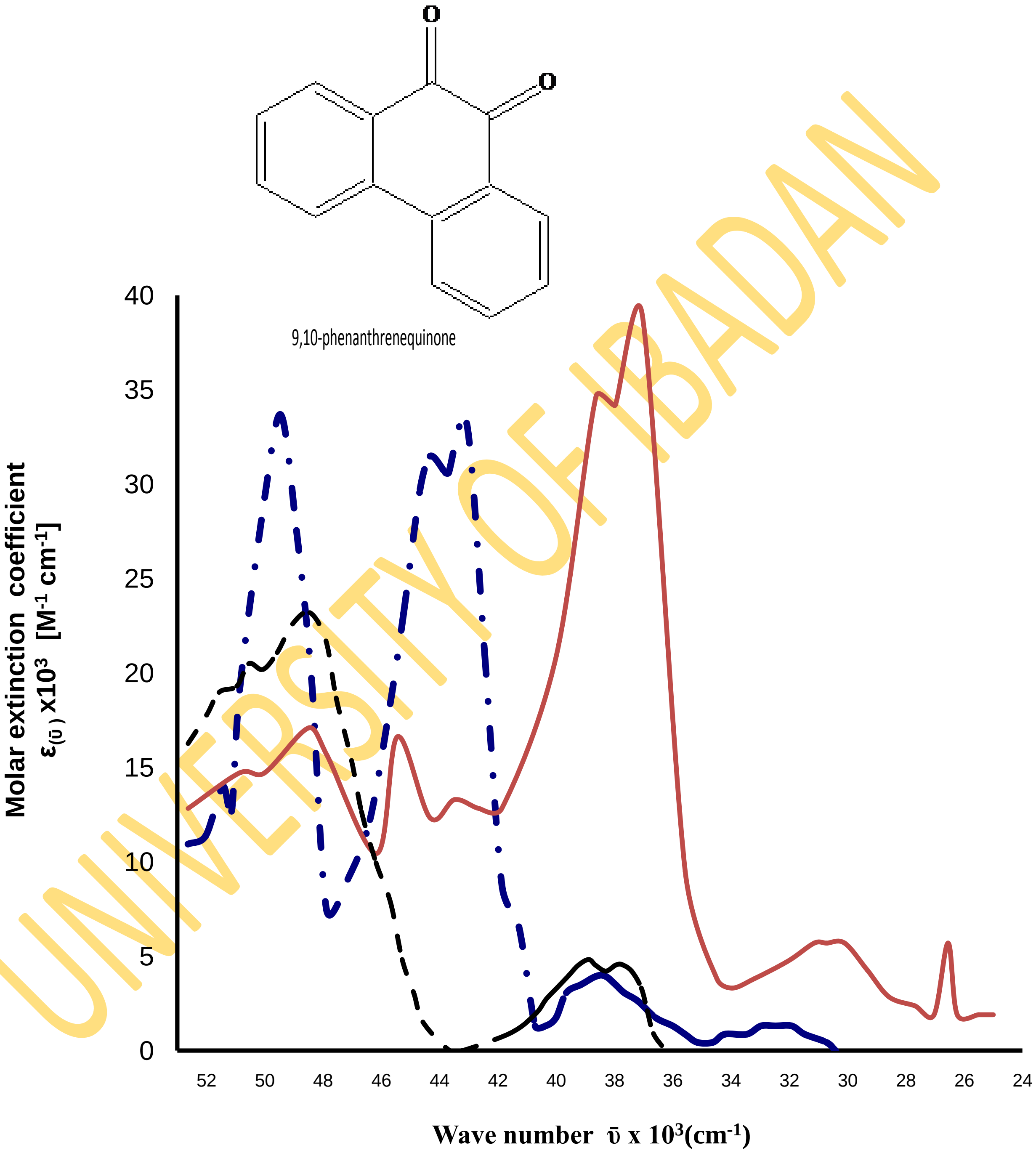


Figure 4.2: Electronic absorption spectra of 9,10-phenanthrenequinone in methanol (-.-.-), dichloromethane (__) and n-heptane(- - -)

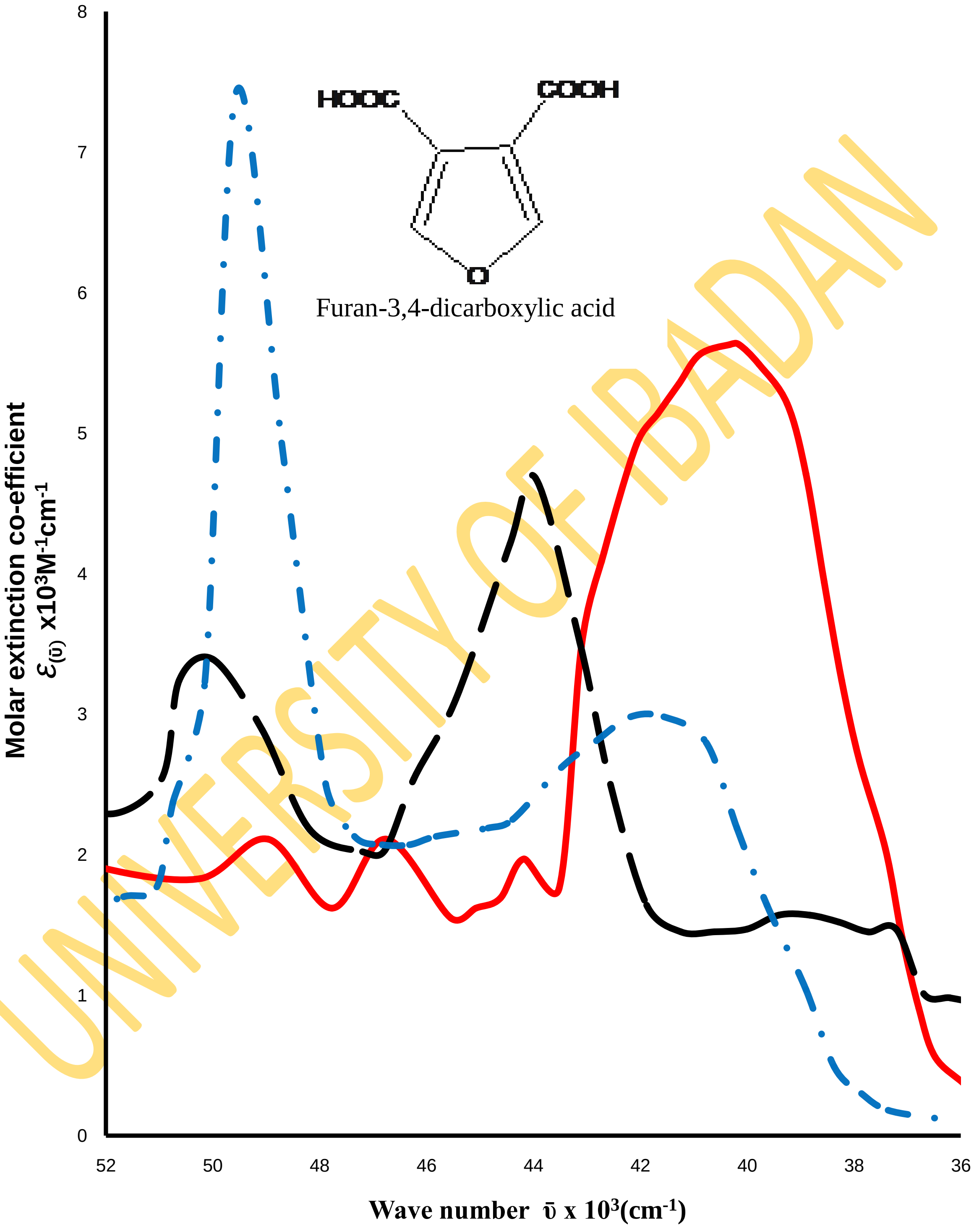


Figure 4.3: Electronic absorption spectra of furan-3,4-dicarboxylic acid in methanol (-.-.-), dichloromethane (___) and n-heptane(- - - -)

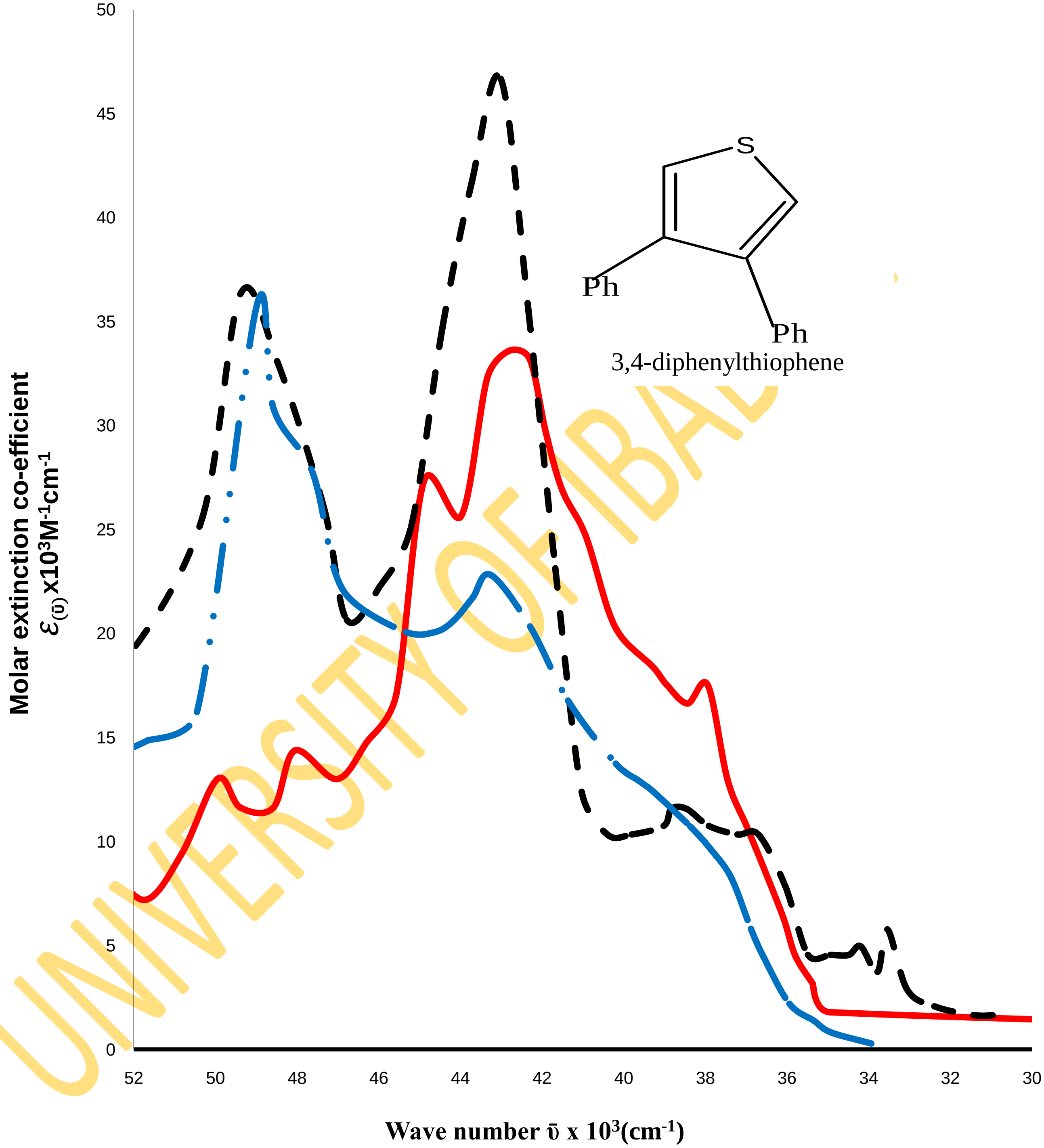


Figure 4.4: Electronic absorption spectra of 3, 4- diphenylthiophene in methanol (-..-..), dichloromethane (____) and n-heptane (- - -)

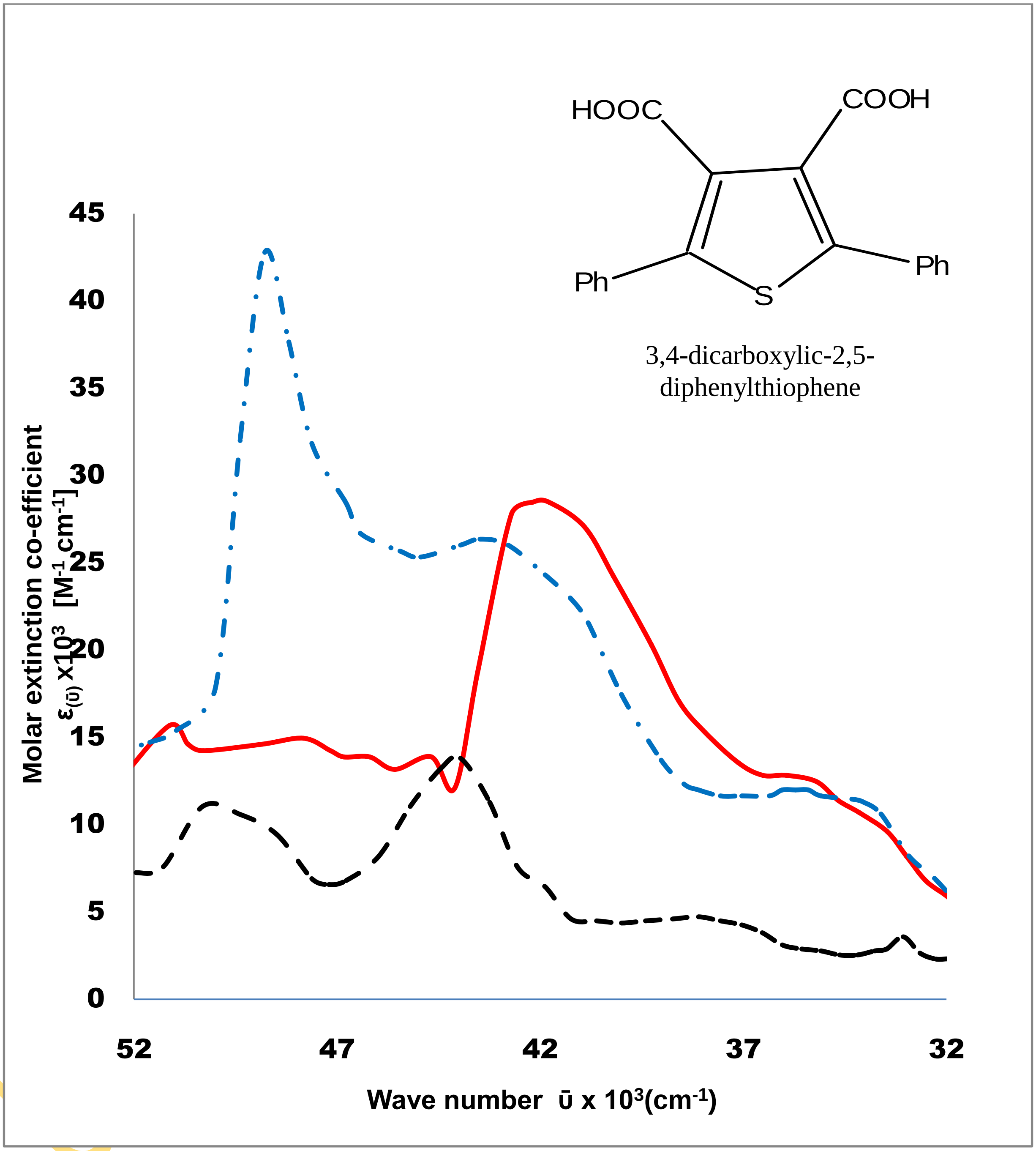
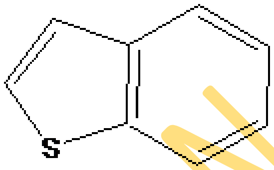


Figure 4.5: Electronic absorption spectra of 3,4-dicarboxylic-2,5-diphenylthiophene in methanol (-. -.-), dichloromethane (___) and n-heptane (- - -)



benzo[b]thiophene

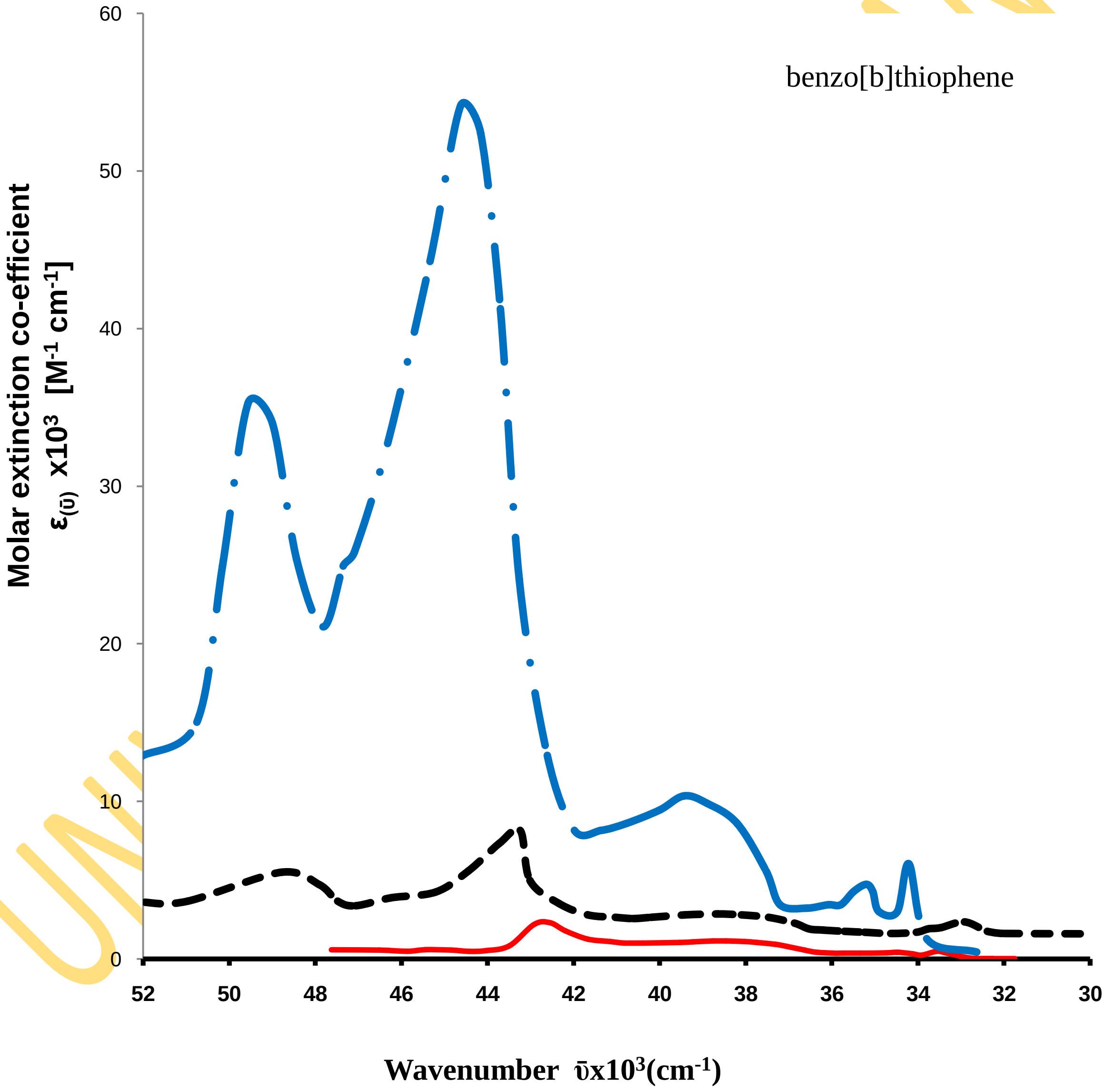
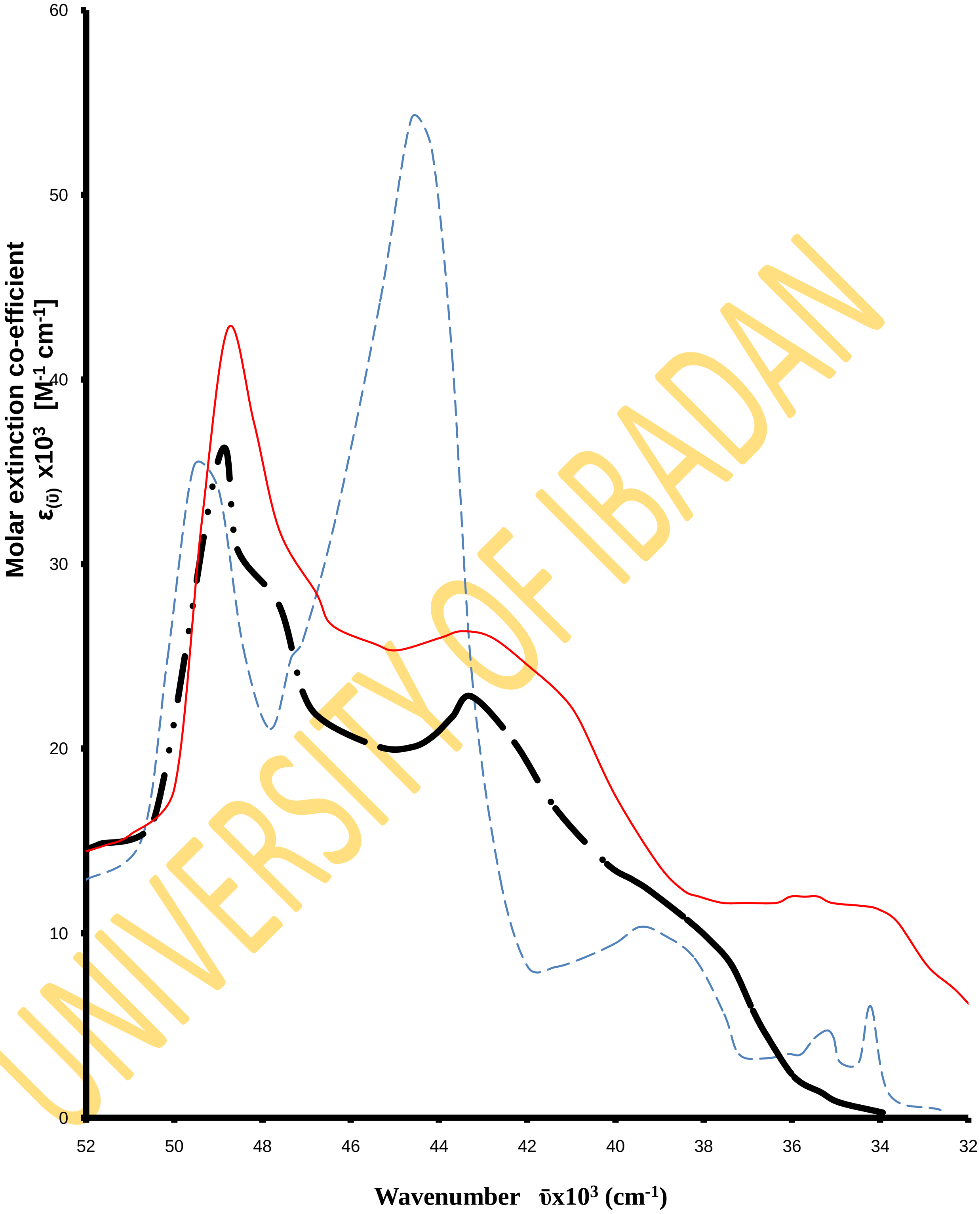


Figure 4.6: Electronic absorption spectra of benzo[b]thiophene in methanol (-.-.-), dichloromethane (____) and n-heptane (- - -)



Wavenumber ῡx10^3 (cm^{-1})

Figure 4.7: Electronic absorption spectra of 3,4-dicarboxylic-2,5-diphenylthiophene (__), benzo[b]thiophene (- - -), and 3,4-diphenyithiophene (-..-..) in methanol

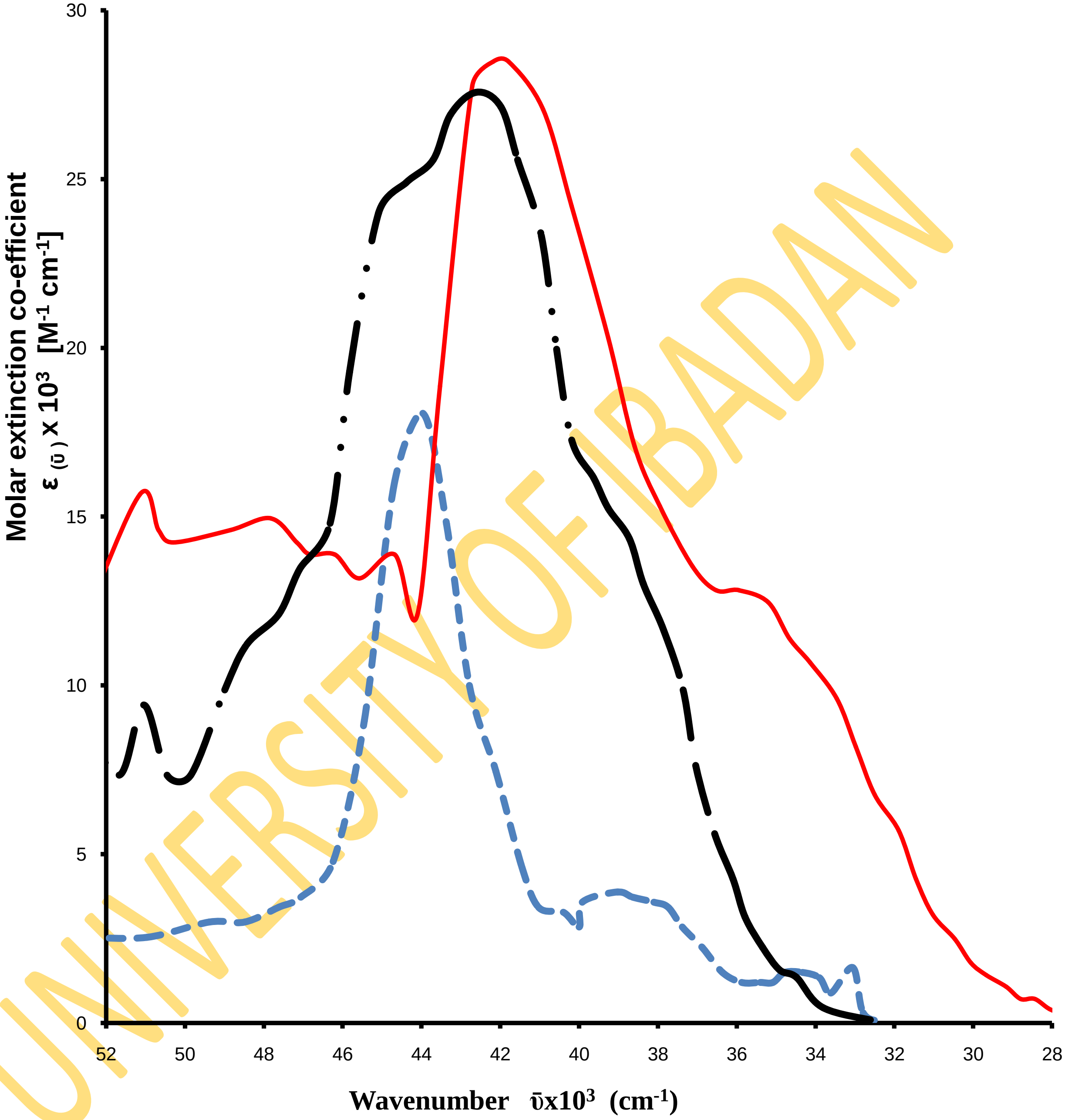


Figure 4.8: Electronic absorption spectra of 3,4-dicarboxylic-2,5-diphenylthiophene (__), benzo[b]thiophene (- - -) and 3,4-diphenyithiophene (-..-..) in dichloromethane

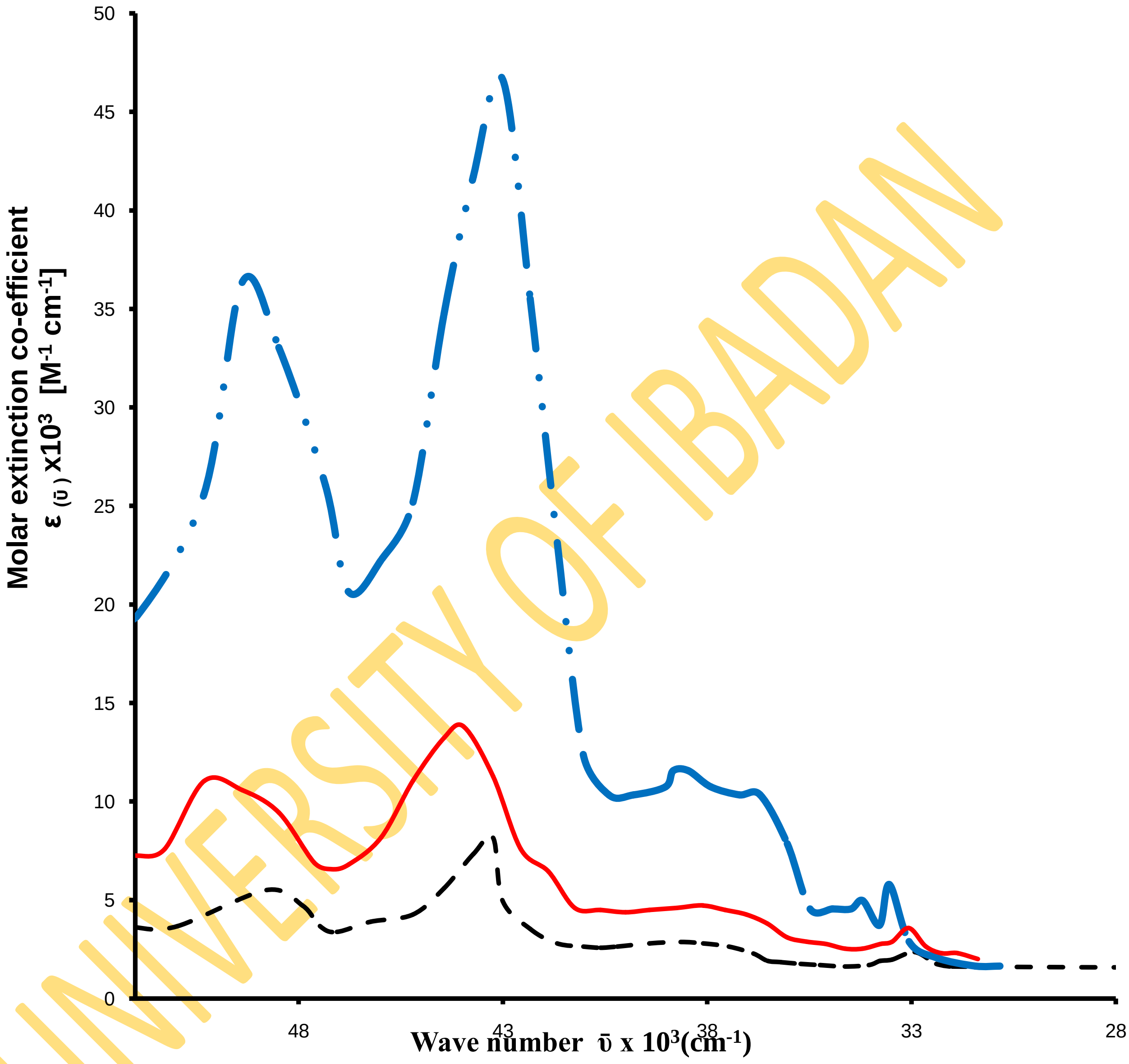


Figure 4.9: Electronic absorption spectra of 3,4 dicarboxylic-2,5-diphenylthiophene (___), benzo[b]thiophene (-.. -..) and 3,4-diphenyithiophene (- - -) in n- heptane

Table 4.1: Summary of observed absorption bands of Compounds in different solvent

Compounds and Transitions	Methanol		Ethanol		Tetrahydrofuran		Acetonitrile	
	$\bar{\nu}_{max}$ (cm^{-1})	ε_{max} $M^{-1} cm^{-1}$	$\bar{\nu}_{max}$ (cm^{-1})	ε_{max} $M^{-1} cm^{-1}$	$\bar{\nu}_{max}$ (cm^{-1})	ε_{max} $M^{-1} cm^{-1}$	$\bar{\nu}_{max}$ (cm^{-1})	ε_{max} $M^{-1} cm^{-1}$
DPT								
$S_0 \rightarrow S_1$	-	-	-	-	-	-	-	-
$S_0 \rightarrow S_2$	39,063	12,535	35,492	15,766	-	-	39,216	12,980
$S_0 \rightarrow S_3$	43,103	23,103	42,373	38,502	42,553	36,592	42,918	23,260
$S_0 \rightarrow S_4$	49,020	36,285	47,170	21,084	47,170	44,439	-	-
$S_0 \rightarrow S_5$	-	-	-	-	-	-	-	-
DCDPT								
$S_0 \rightarrow S_1$	-	-	-	-	-	-	-	-
$S_0 \rightarrow S_2$	35,714	11,315	35,461	9,672	35,842	23,615	35,714	5,937
$S_0 \rightarrow S_3$	43,103	25,975	42,373	22,229	43,290	56,562	43,860	14,281
$S_0 \rightarrow S_4$	49,020	42,088	48,387	10,181	47,393	76,358	48,485	8,555
BT								
$S_0 \rightarrow S_1$	33,784	5,754	34,176	1,934	33,557	1,618	33,557	1,611
$S_0 \rightarrow S_2$	34,722	3,274	34,662	1,654	34,483	1,442	34,551	1,443
$S_0 \rightarrow S_3$	39,063	10,000	38,168	6,082	40,000	3,869	38,760	3,871
$S_0 \rightarrow S_4$	44,248	52,480	43,860	22,620	44,053	12,153	43,478	17,719
$S_0 \rightarrow S_5$	49,505	33,925	47,170	60,549	-	-	-	-

Table 4.1 (continued): Summary of observed absorption bands of compounds in different solvent

Compounds and Transitions	Methanol		Ethanol		Tetrahydrofuran		Acetonitrile	
	$\bar{\nu}_{max}\,(cm^{-1})$	ε_{max} $M^{-1}\,cm^{-1}$	$\bar{\nu}_{max}\,(cm^{-1})$	ε_{max} $M^{-1}\,cm^{-1}$	$\bar{\nu}_{max}\,(cm^{-1})$	ε_{max} $M^{-1}\,cm^{-1}$	$\bar{\nu}_{max}\,(cm^{-1})$	ε_{max} $M^{-1}\,cm^{-1}$
DCF								
$S_0 \rightarrow S_1$	-	-	-	-	-	-	-	-
$S_0 \rightarrow S_2$	-	-	-	-	34,483	389	-	-
$S_0 \rightarrow S_3$	41,667	2,976	41,322	3,169	41,840	3,662	41,152	54,944
$S_0 \rightarrow S_4$	49,505	7,445	48,678	6,752	47,170	3,379	-	-
DPCP								
$S_0 \rightarrow S_1$	-	-	-	-	28,986	1,428	31,949	1,125
$S_0 \rightarrow S_2$	33,557	2,154	33,557	39,649	33,223	26,830	33,786	21,803
$S_0 \rightarrow S_3$	45,455	1,305	45,455	32,122	45,249	20,032	35,842	24,542
$S_0 \rightarrow S_4$	49,505	1,396	-	-	-	-	-	-
PQ								
$S_0 \rightarrow S_1$	24,038	1,006	23,810	3,057	25,381	4,805	24,331	4,810
$S_0 \rightarrow S_2$	31,056	3,891	30,864	9,492	32,787	12,449	31,397	6,121
$S_0 \rightarrow S_3$	37,594	32,530	37,594	71,109	37,594	80,808	37,736	46,892
$S_0 \rightarrow S_4$	38,671	29,994	-	-	38,917	82,337	38,911	43,176
$S_0 \rightarrow S_5$	47,170	32,880	46,235	41,185	47,170	92,601	46,083	29,076

Table 4.1 (continued): Summary of observed absorption bands of Compounds in different solvent

Compounds and Transitions	1,2- dichloroethane		Dichloromethane		Cyclohexane		n-Heptane	
	$\bar{\nu}_{max}\ (cm^{-1})$	ε_{max} $M^{-1}cm^{-1}$	$\bar{\nu}_{max}\ (cm^{-1})$	ε_{max} $M^{-1}cm^{-1}$	$\bar{\nu}_{max}\ (cm^{-1})$	ε_{max} $M^{-1}cm^{-1}$	$\bar{\nu}_{max}\ (cm^{-1})$	ε_{max} $M^{-1}cm^{-1}$
DPT								
$S_0 \rightarrow S_1$	-	-	-	-	31,769	8,021	33,784	5,947
$S_0 \rightarrow S_2$	39,063	15,879	38,911	5,474	33,333	14,681	34,722	4,956
$S_0 \rightarrow S_3$	42,735	33,464	42,373	35,688	34,510	13,027	39,370	11,399
$S_0 \rightarrow S_4$	-	-	-	-	44,643	11,786	44,248	46,091
$S_0 \rightarrow S_5$	-	-	-	-	49,505	19,148	50,000	35,931
DCDPT								
$S_0 \rightarrow S_1$	-	-	-	-	-	-	33,786	3,589
$S_0 \rightarrow S_2$	34,247	26,283	35,336	6,453	-	-	39,063	4,693
$S_0 \rightarrow S_3$	44,248	66,305	42,077	14,093	44,622	12,220	44,248	13,665
$S_0 \rightarrow S_4$	-	-	-	-	50,000	11,092	50,000	10,836
BT								
$S_0 \rightarrow S_1$	33,557	1,675	33,298	1,222	-	-	33,540	2,350
$S_0 \rightarrow S_2$	34,772	1,675	34,602	1022	-	-	38,460	2,860
$S_0 \rightarrow S_3$	39,063	3,958	38,960	2,822	43,860	3,730	43,240	8,150
$S_0 \rightarrow S_4$	43,860	18,472	42,553	16,550	49,920	7,630	49,780	5,510

Table 4.1 (continued): Summary of observed absorption bands of compounds in different solvent

Compounds and Transitions	1,2- dichloroethane		dichloromethane		Cyclohexane		n-Heptane	
	$\bar{\nu}_{max}$ (cm^{-1})	ε_{max} M^{-1} cm^{-1}	$\bar{\nu}_{max}$ (cm^{-1})	ε_{max} M^{-1} cm^{-1}	$\bar{\nu}_{max}$ (cm^{-1})	ε_{max} M^{-1} cm^{-1}	$\bar{\nu}_{max}$ (cm^{-1})	ε_{max} M^{-1} cm^{-1}
DCF								
$S_0 \rightarrow S_1$	-	-	-	-	-	-	33,784	1,217
$S_0 \rightarrow S_2$	-	-	-	-	-	-	39,063	1,544
$S_0 \rightarrow S_3$	40,650	4,401	40,650	5,789	-	-	44,248	4,680
$S_0 \rightarrow S_4$					50,000	18,479	50,000	3,346
DPCP								
$S_0 \rightarrow S_1$	31,884	5,860	32,051	4,814	-	-	-	-
$S_0 \rightarrow S_2$	-	-	-	-	38,906	10,569	33,784	6,615
$S_0 \rightarrow S_3$	35,714	25,832	35,461	20,355	42,373	25,930	44,248	8,641
$S_0 \rightarrow S_4$	44,248	16,504	43,234	10,895	49,505	55,101	50,000	8,462
PQ								
$S_0 \rightarrow S_1$	-	-	-	-	-	-	-	-
$S_0 \rightarrow S_2$	31,250	4,172	30,960	5,897	-	-	-	-
$S_0 \rightarrow S_3$	37,594	30,644	37,313	38,111	-	-	-	-
$S_0 \rightarrow S_4$	-	-	-	-	38,760	12,946	38,760	4,781
$S_0 \rightarrow S_5$	45,045	14,962	-	-	49,505	36,706	48,544	24,048

Table 4.2: Summary of oscillator strength in solution and vapour phase for the observed bands in different solvents

Compounds and Transitions	Methanol		Ethanol		Tetrahydrofuran	
	$f_{(s)}$	$f_{(v)}$	$f_{(s)}$	$f_{(v)}$	$f_{(s)}$	$f_{(v)}$
DPT						
$S_0 \rightarrow S_1$	-	-	-	-	-	-
$S_0 \rightarrow S_2$	0.23	0.23	0.23	0.22	0.84	0.83
$S_0 \rightarrow S_3$	0.54	0.41	0.62	0.60	0.47	0.46
$S_0 \rightarrow S_4$	0.53	0.51	1.78	1.33	-	-
DCDPT						
$S_0 \rightarrow S_1$	-	-	-	-	-	-
$S_0 \rightarrow S_2$	0.30	0.29	0.24	0.24	0.42	0.41
$S_0 \rightarrow S_3$	0.43	0.42	0.58	0.57	1.07	1.05
$S_0 \rightarrow S_4$	0.65	0.63	0.43	0.42	0.79	0.78
BT						
$S_0 \rightarrow S_1$	0.013	0.013	0.0054	0.0052	0.0031	0.003
$S_0 \rightarrow S_2$	0.02	0.019	0.0075	0.0073	0.0065	0.064
$S_0 \rightarrow S_3$	0.13	0.13	0.075	0.073	0.051	0.05
$S_0 \rightarrow S_4$	0.71	0.69	0.10	0.1	0.2	0.19
$S_0 \rightarrow S_5$	0.40	0.39	0.92	0.9	-	-
DCF						
$S_0 \rightarrow S_1$	-	-	-	-	-	-
$S_0 \rightarrow S_2$	-	-	-	-	0.0045	0.004
$S_0 \rightarrow S_3$	0.092	0.089	0.076	0.074	0.075	0.074
$S_0 \rightarrow S_4$	0.059	0.057	0.091	0.089	0.038	0.037
DPCP						
$S_0 \rightarrow S_1$	-	-	-	-	0.014	0.014
$S_0 \rightarrow S_2$	0.038	0.037	0.79	0.77	0.50	0.49
$S_0 \rightarrow S_3$	0.023	0.022	0.80	0.78	0.37	0.36
$S_0 \rightarrow S_4$	0.018	0.017	-	-	-	-

Table 4.2 (continued): Summary of oscillator strength in solution and vapour phase for the observed bands in different solvents

Compounds and Transitions	Acetonitrile		1,2-dichloro ethane		Dichloroethane	
	$f_{(s)}$	$f_{(v)}$	$f_{(s)}$	$f_{(v)}$	$f_{(s)}$	$f_{(v)}$
DPT						
$S_0 \rightarrow S_1$	-	-	-	-	-	-
$S_0 \rightarrow S_2$	0.21	0.21	0.34	0.33	0.49	0.49
$S_0 \rightarrow S_3$	0.38	0.33	-	-	0.70	0.70
$S_0 \rightarrow S_4$	-	-	0.72	0.71	-	-
DCDPT						
$S_0 \rightarrow S_1$	-	-	-	-	-	-
$S_0 \rightarrow S_2$	0.25	0.24	0.31	0.30	0.13	0.13
$S_0 \rightarrow S_3$	0.73	0.71	1.55	1.55	0.32	0.31
$S_0 \rightarrow S_4$	0.46	0.45	-	-	-	-
BT						
$S_0 \rightarrow S_1$	0.00032	0.00031	0.0045	0.0044	0.010	0.0099
$S_0 \rightarrow S_2$	0.0055	0.0053	0.011	0.011	0.015	0.015
$S_0 \rightarrow S_3$	0.45	0.44	0.046	0.045	0.011	0.10
$S_0 \rightarrow S_4$	0.14	0.14	0.19	0.19	0.10	0.098
DCF						
$S_0 \rightarrow S_1$	-	-	-	-	-	-
$S_0 \rightarrow S_2$	-	-	-	-	-	-
$S_0 \rightarrow S_3$	0.12	0.12	0.13	0.12	0.033	0.032
$S_0 \rightarrow S_4$	-	-	-	-	-	-
DPCP						
$S_0 \rightarrow S_1$	0.004	0.004	0.022	0.022	0.034	0.033
$S_0 \rightarrow S_2$	0.19	0.18	-	-	-	-
$S_0 \rightarrow S_3$	0.34	0.34	0.45	0.45	0.37	0.36
$S_0 \rightarrow S_4$	-	-	0.23	0.22	0.13	0.12
PQ						
$S_0 \rightarrow S_1$	0.018	0.017	-	-	-	-
$S_0 \rightarrow S_2$	0.10	0.098	0.065	0.064	0.093	0.091
$S_0 \rightarrow S_3$	0.41	0.40	0.48	0.48	0.71	0.69
$S_0 \rightarrow S_4$	0.59	0.57	-	-	-	-
$S_0 \rightarrow S_5$	0.23	0.22	0.15	0.15	-	-

Table 4.2 (continued): Summary of oscillator strength in solution and vapour phase for the observed bands in different solvents

Compounds and Transitions	**Cyclohexane**		**1,2-dichloro ethane**	
	$f_{(s)}$	$f_{(v)}$	$f_{(s)}$	$f_{(v)}$
DPT				
$S_0 \rightarrow S_1$	0.058	0.057	0.021	0.020
$S_0 \rightarrow S_2$	0.14	0.14	0.027	0.026
$S_0 \rightarrow S_3$	0.16	0.15	0.18	0.18
$S_0 \rightarrow S_4$	0.18	0.18	0.70	0.63
$S_0 \rightarrow S_5$	0.30	0.30	0.61	0.60
DCDPT				
$S_0 \rightarrow S_1$	-	-	0.030	0.029
$S_0 \rightarrow S_2$	-	-	0.095	0.093
$S_0 \rightarrow S_3$	-	-	0.23	0.22
$S_0 \rightarrow S_4$	0.18	0.18	0.15	0.15
BT				
$S_0 \rightarrow S_1$	-	-	0.0082	0.0081
$S_0 \rightarrow S_2$	-	-	0.0092	0.0090
$S_0 \rightarrow S_3$	0.0031	0.0030	0.042	0.041
$S_0 \rightarrow S_4$	0.0087	0.0086	0.023	0.022
DCF				
$S_0 \rightarrow S_1$	-	-	0.011	0.011
$S_0 \rightarrow S_2$	-	-	0.028	0.027
$S_0 \rightarrow S_3$	-	-	0.042	0.041
$S_0 \rightarrow S_4$	0.20	0.20	0.045	0.044
DPCP				
$S_0 \rightarrow S_1$	-	-	-	-
$S_0 \rightarrow S_2$	0.11	0.11	0.16	0.580
$S_0 \rightarrow S_3$	0.37	0.36	0.15	0.14
$S_0 \rightarrow S_4$	1.13	1.13	0.013	0.013
PQ				
$S_0 \rightarrow S_1$	-	-	-	-
$S_0 \rightarrow S_2$	-	-	-	-
$S_0 \rightarrow S_3$	-	-	-	-
$S_0 \rightarrow S_4$	0.15	0.15	0.065	0.064
$S_0 \rightarrow S_5$	0.78	0.77	0.48	0.47

Table 4.3: **Summary of the calculated ground state polarizabilities α ($\mathring{A}^3$) of the compounds studied in various solvents**

Compounds and Transitions	Methanol (x10^{-2})	Ethanol (x10^{-2})	Tetra-hydrofuran (x10^{-2})	Acetonitrile (x10^{-2})
DPT				
$S_0 \rightarrow S_1$	-	-	-	-
$S_0 \rightarrow S_2$	4.69	2.27	16.50	9.75
$S_0 \rightarrow S_3$	0.86	6.14	9.23	15.40
$S_0 \rightarrow S_4$	10.6	17.70	-	-
$S_0 \rightarrow S_5$	-	-	-	-
DCDPT				
$S_0 \rightarrow S_1$	-	-	-	-
$S_0 \rightarrow S_2$	7.15	6.88	6.43	5.95
$S_0 \rightarrow S_3$	10.20	16.60	16.60	17.50
$S_0 \rightarrow S_4$	15.40	12.05	12.30	11.10
BT				
$S_0 \rightarrow S_1$	0.14	0.07	0.18	0.77
$S_0 \rightarrow S_2$	0.21	0.10	0.37	0.13
$S_0 \rightarrow S_3$	1.40	1.01	2.87	10.80
$S_0 \rightarrow S_4$	7.56	10.20	11.20	3.36
$S_0 \rightarrow S_5$	4.24	91.70	-	-
DCF				
$S_0 \rightarrow S_1$	-	-	-	-
$S_0 \rightarrow S_2$	-	-	0.65	-
$S_0 \rightarrow S_3$	9.63	7.87	10.9	16.60
$S_0 \rightarrow S_4$	6.17	9.63	5.50	-
DPCP				
$S_0 \rightarrow S_1$	-	-	0.36	0.16
$S_0 \rightarrow S_2$	10.0	0.11	12.7	7.60
$S_0 \rightarrow S_3$	6.06	0.12	9.44	14.10
$S_0 \rightarrow S_4$	4.74	-	-	-
PQ				
$S_0 \rightarrow S_1$	0.02	0.33	4.82	0.29
$S_0 \rightarrow S_2$	0.94	1.38	1.67	1.68
$S_0 \rightarrow S_3$	4.53	12.6	5.91	6.74
$S_0 \rightarrow S_4$	7.14	-	7.16	9.71
$S_0 \rightarrow S_5$	8.31	8.69	7.48	3.74

Table 4.3 (continued): Summary of the calculated ground state polarizabilities α (Å^3) of the compounds studied in various solvents

Compounds and Transitions	1,2-dichloro Ethane (x10^{-2})	Dichloro Methane (x10^{-2})	Cyclohexane (x10^{-2})	n-heptane (x10^{-2})
DPT				
$S_0 \rightarrow S_1$	-	-	2.13	0.45
$S_0 \rightarrow S_2$	13.70	6.01	5.16	0.58
$S_0 \rightarrow S_3$	6.42	8.59	5.71	3.90
$S_0 \rightarrow S_4$	-	-	6.70	14.00
$S_0 \rightarrow S_5$	-	-	11.10	13.20
DCDPT				
$S_0 \rightarrow S_1$	-	-	-	1.90
$S_0 \rightarrow S_2$	4.58	5.78	-	19.00
$S_0 \rightarrow S_3$	23.00	14.20	-	45.20
$S_0 \rightarrow S_4$	-	-	30.80	29.80
BT				
$S_0 \rightarrow S_1$	1.47	0.50	-	0.33
$S_0 \rightarrow S_2$	3.50	0.73	-	0.36
$S_0 \rightarrow S_3$	14.90	5.23	4.50	3.27
$S_0 \rightarrow S_4$	63.0	4.94	13.00	2.50
DCF				
$S_0 \rightarrow S_1$	-	-	-	1.86
$S_0 \rightarrow S_2$	-	-	-	4.73
$S_0 \rightarrow S_3$	13.30	9.64	20.30	7.10
$S_0 \rightarrow S_4$	-	-		7.61
DPCP				
$S_0 \rightarrow S_1$	0.31	0.80	-	-
$S_0 \rightarrow S_2$	6.50	-	1.87	14.2
$S_0 \rightarrow S_3$	3.20	8.90	6.19	12.8
$S_0 \rightarrow S_4$	-	3.00	18.80	1.15
PQ				
$S_0 \rightarrow S_1$	-	-	-	-
$S_0 \rightarrow S_2$	1.64	1.50	-	-
$S_0 \rightarrow S_3$	12.1	11.4	-	-
$S_0 \rightarrow S_4$	-	-	4.90	3.41
$S_0 \rightarrow S_5$	3.88	-	25.90	25.00

Table 4.4: **Experimental transition polarizabilities $\Delta\alpha$ (Å^3) and transition dipole $\Delta\mu$ (D) moments for 3,4-diphenylthiophene in various solvents by applying equations 3.3 and 3.5 of section 3.3.4**

Solvents	$\Delta\alpha$ x10^{-2} (Å^3)	$\Delta\mu(D)$
Methanol		
$S_0 \rightarrow S_1$	-	-
$S_0 \rightarrow S_2$	7.85	0.48
$S_0 \rightarrow S_3$	14.30	0.65
	17.80	0.73
$S_0 \rightarrow S_4$	-	-
Ethanol		
$S_0 \rightarrow S_1$	-	-
$S_0 \rightarrow S_2$	2.27	0.48
$S_0 \rightarrow S_3$	6.14	0.79
	17.70	1.73
$S_0 \rightarrow S_4$	-	-

Table 4.5: **Experimental transition polarizabilities Δα (Å^3) and transition dipole Δμ (D) moments for 3,4- dicarboxylic-2,5-diphenylthiophene in various solvents of choice by applying equations3.2 and 3.5 of section 3.3.4**

Solvent	$\Delta\alpha$ x10^{-2} ($\AA^3$)	$\Delta\mu(D)$
Methanol		
$S_0 \rightarrow S_1$	-	-
$S_0 \rightarrow S_2$	10.90	0.55
$S_0 \rightarrow S_3$	15.60	0.66
$S_0 \rightarrow S_4$	23.50	0.81
Ethanol		
$S_0 \rightarrow S_1$	-	-
$S_0 \rightarrow S_2$	5.77	0.49
$S_0 \rightarrow S_3$	13.90	0.76
$S_0 \rightarrow S_4$	10.30	0.66
Tetrahydrofuran		
$S_0 \rightarrow S_1$	-	-
$S_0 \rightarrow S_2$	3.64	0.65
$S_0 \rightarrow S_3$	9.41	1.04
$S_0 \rightarrow S_4$	6.95	0.89
Acetonitrile		
$S_0 \rightarrow S_1$	-	-
$S_0 \rightarrow S_2$	5.95	0.50
$S_0 \rightarrow S_3$	17.50	0.85
$S_0 \rightarrow S_4$	11.10	0.68

Table 4.6: Experimental transition polarizabilities $\Delta\alpha$ ($\mathring{A}^3$) and transition dipole moments $\Delta\mu$ (D) for 2,3-diphenylcyclopropenone in various solvents of choice by applying equations 3.3 and 3.5 of section 3.3.4

Solvent	$\Delta\alpha$ x10^{-2}($\mathring{A}^3$)	$\Delta\mu(D)$
Methanol		
$S_0 \rightarrow S_1$	-	-
$S_0 \rightarrow S_2$	1.80	0.13
$S_0 \rightarrow S_3$	2.30	0.15
$S_0 \rightarrow S_4$	39.00	0.20
Tetrahydrofuran		
$S_0 \rightarrow S_1$	0.48	0.12
$S_0 \rightarrow S_2$	16.90	0.71
$S_0 \rightarrow S_3$	12.60	0.61
$S_0 \rightarrow S_4$	-	-
Acetonitrile		
$S_0 \rightarrow S_1$	0.15	0.066
$S_0 \rightarrow S_2$	7.00	0.43
$S_0 \rightarrow S_3$	12.90	0.59
$S_0 \rightarrow S_4$	-	-
1,2-dichloroethane		
$S_0 \rightarrow S_1$	3.20	0.48
$S_0 \rightarrow S_2$	-	-
$S_0 \rightarrow S_3$	6.50	0.67
$S_0 \rightarrow S_4$	0.30	0.19
Dichloromethane		
$S_0 \rightarrow S_1$	20.00	0.18
$S_0 \rightarrow S_2$	-	-
$S_0 \rightarrow S_3$	1.26	0.61
$S_0 \rightarrow S_4$	14.0	0.35

Table 4.7: Experimental transition polarizabilities $\Delta\alpha$ (Å^3) and transition dipole moments $\Delta\mu$ (D) for 9,10-phenanthrenequinone in various solvents by applying equations 3.3 and 3.5 of section 3.3.4

Solvents	$\Delta\alpha$ x10^{-2}(Å^3)	$\Delta\mu$(D)
Methanol		
$S_0\rightarrow S_1$	0.048	0.037
$S_0\rightarrow S_2$	2.25	0.25
$S_0\rightarrow S_3$	10.80	0.56
$S_0\rightarrow S_4$	17.10	0.70
$S_0\rightarrow S_5$	19.80	0.75
Ethanol		
$S_0\rightarrow S_1$	0.30	0.20
$S_0\rightarrow S_2$	1.26	0.40
$S_0\rightarrow S_3$	11.5	1.23
$S_0\rightarrow S_4$	-	-
$S_0\rightarrow S_5$	7.90	1.02
Tetrahydrofuran		
$S_0\rightarrow S_1$	0.43	0.26
$S_0\rightarrow S_2$	1.47	0.47
$S_0\rightarrow S_3$	5.21	0.87
$S_0\rightarrow S_4$	6.31	0.97
$S_0\rightarrow S_5$	6.59	0.99
Acetonitrile		
$S_0\rightarrow S_1$	0.26	0.13
$S_0\rightarrow S_2$	1.52	0.32
$S_0\rightarrow S_3$	6.09	0.64
$S_0\rightarrow S_4$	0.88	0.77
$S_0\rightarrow S_5$	3.38	0.47
1,2-dichloroethane		
$S_0\rightarrow S_1$	-	-
$S_0\rightarrow S_2$	71.00	0.26
$S_0\rightarrow S_3$	95.00	0.69
$S_0\rightarrow S_4$	-	-
$S_0\rightarrow S_5$	87.60	0.39

Table 4.8: Experimental transition polarizabilities $\Delta\alpha$ (Å^3) and transition dipole moments $\Delta\mu$ (D) for furan-3,4-dicarboxylic acid in various solvents by applying equations 3.3 and 3.5 of section 3.3.4

Solvents	$\Delta\alpha$ (Å^3)	$\Delta\mu(D)$
Tetrahydrofuran		
$S_0 \rightarrow S_1$	-	-
$S_0 \rightarrow S_2$	0.027	0.063
$S_0 \rightarrow S_3$	5.50	0.27
$S_0 \rightarrow S_4$	0.23	0.20

Table 4.9: **Experimental transition polarizabilities $\Delta\alpha$ ($\acute{A}^3$) and transition dipole moments $\Delta\mu$ (D) for benzo[b]thiophene in various solvents by applying equations 3.3 and 3.5 of section 3.3.4**

Solvents	$\Delta\alpha$ x10^{-2} ($\acute{A}^3$)	$\Delta\mu$(D)
Methanol		
$S_0 \rightarrow S_1$	0.41	0.11
$S_0 \rightarrow S_2$	0.63	0.41
$S_0 \rightarrow S_3$	4.13	0.36
$S_0 \rightarrow S_4$	22.30	0.84
$S_0 \rightarrow S_5$	12.50	0.63
Ethanol		
$S_0 \rightarrow S_1$	0.14	0.071
$S_0 \rightarrow S_2$	0.20	0.087
$S_0 \rightarrow S_3$	2.04	0.27
$S_0 \rightarrow S_4$	2.76	0.31
$S_0 \rightarrow S_5$	0.25	0.95
Tetrahydrofuran		
$S_0 \rightarrow S_1$	0.71	0.055
$S_0 \rightarrow S_2$	1.52	0.26
$S_0 \rightarrow S_3$	0.12	0.22
$S_0 \rightarrow S_4$	0.46	0.44
Acetonitrile		
$S_0 \rightarrow S_1$	0.008	0.0057
$S_0 \rightarrow S_2$	0.18	0.074
$S_0 \rightarrow S_3$	15.10	0.67
$S_0 \rightarrow S_4$	4.70	0.37
1,2-dichloroethane		
$S_0 \rightarrow S_1$	0.35	0.067
$S_0 \rightarrow S_2$	0.84	0.010
$S_0 \rightarrow S_3$	3.59	0.21
$S_0 \rightarrow S_4$	15.20	0.44

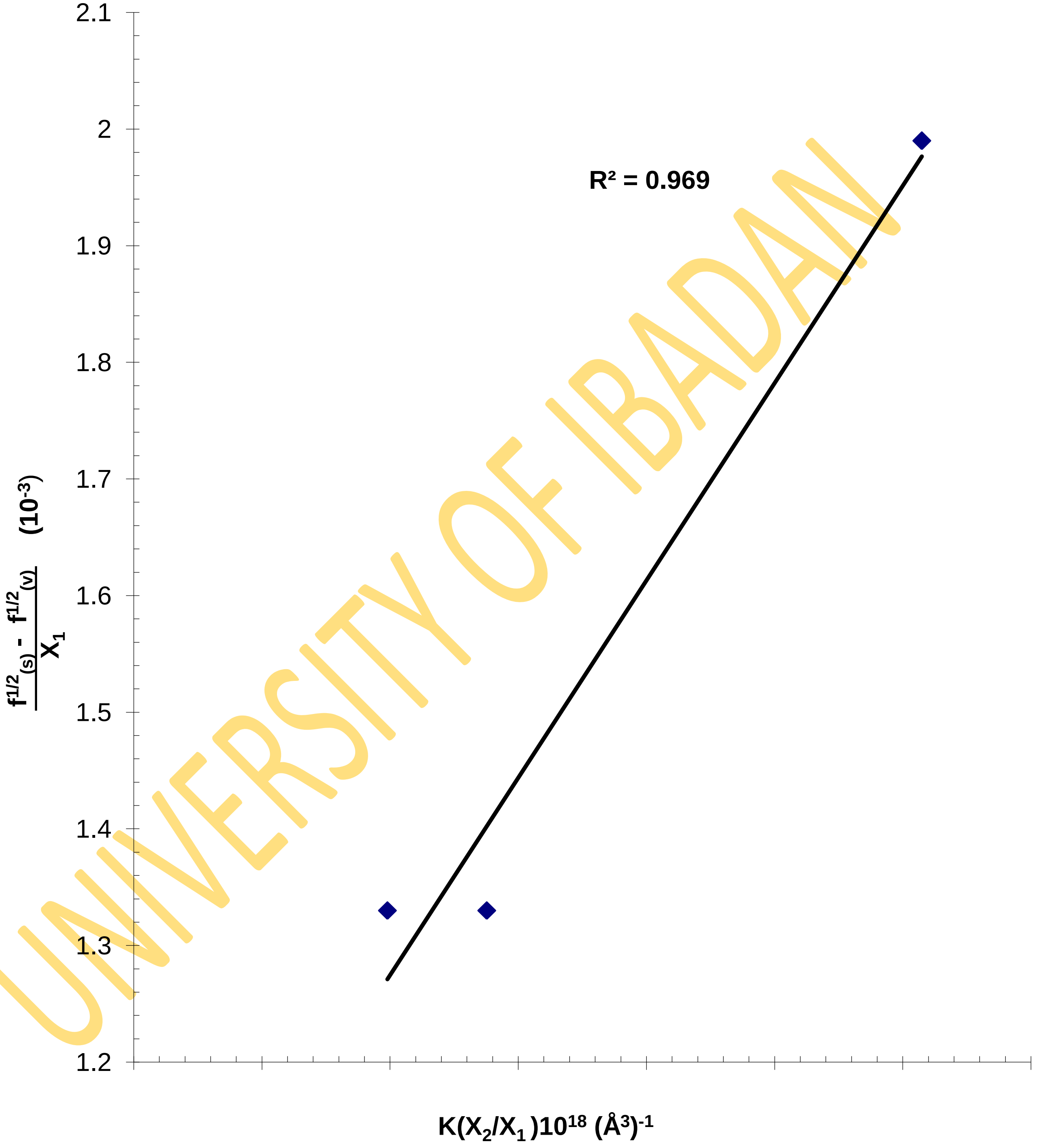


Fig 4.10a: **Plots of data on intensity perturbation of the bands of 2,3-diphenylcyclopropenone in methanol**

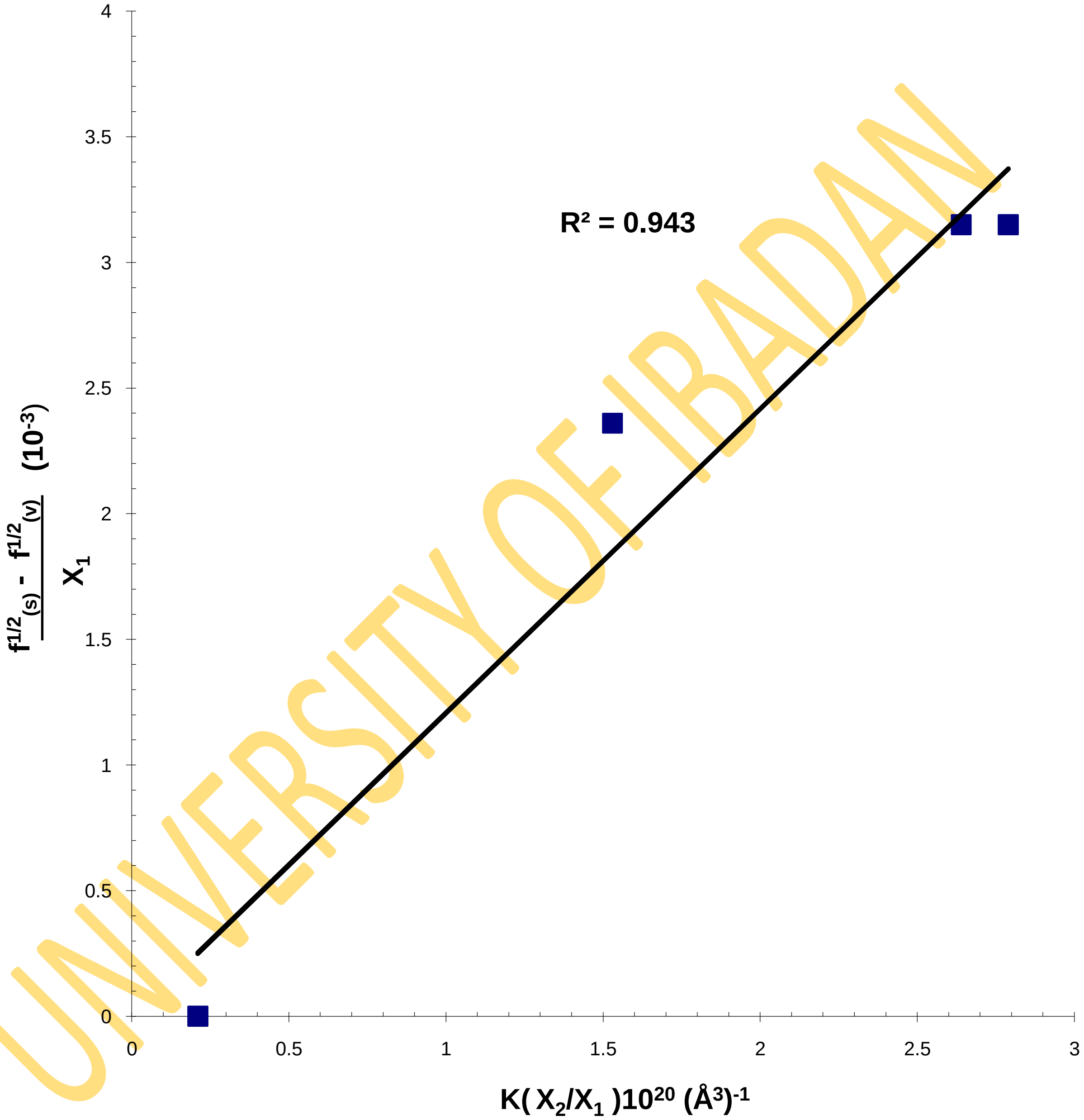


Fig 4.10b.:Plots of data on intensity perturbation of the bands of 2,3-diphenylcyclopropenone in dichloromethane

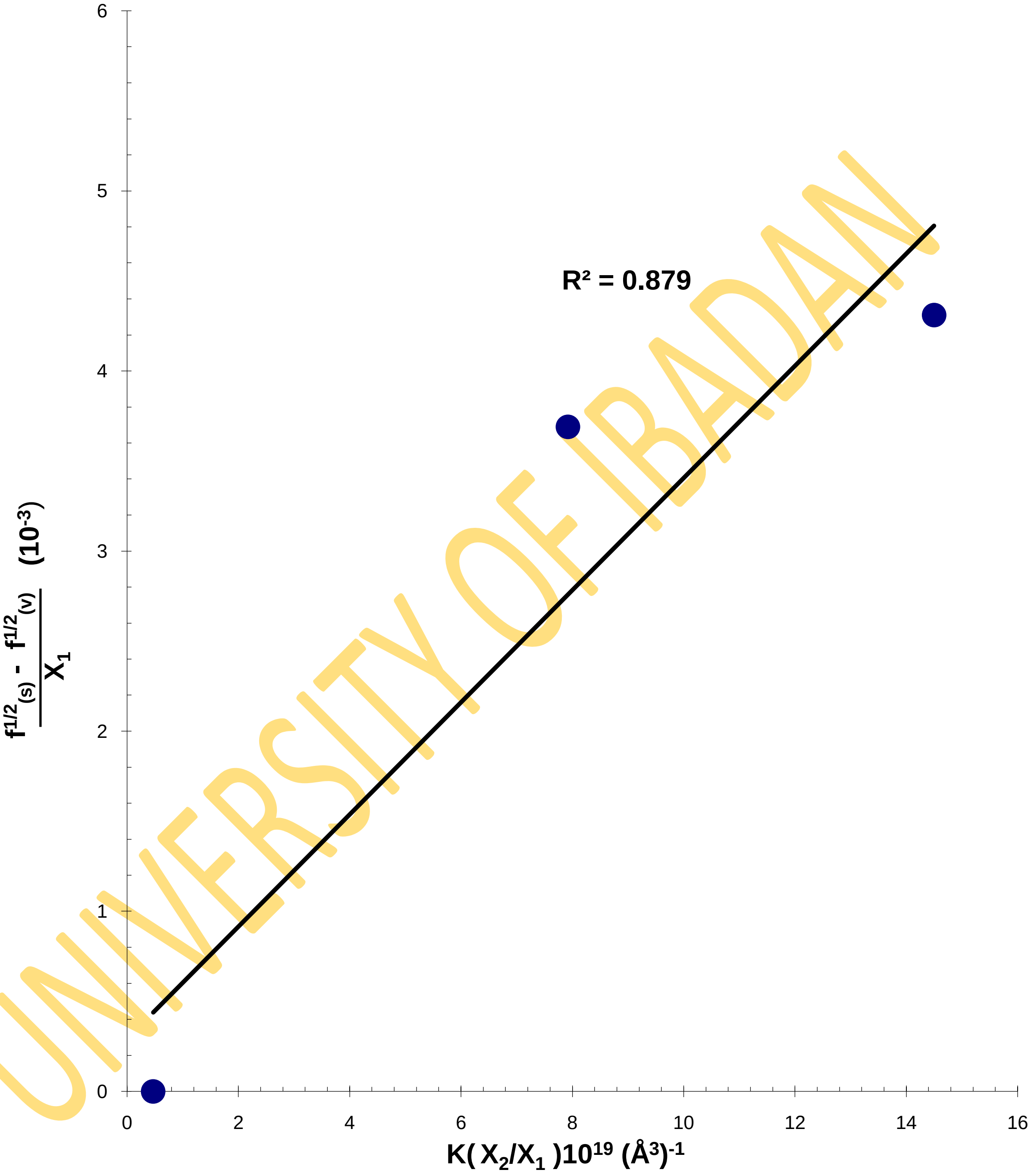


Fig 4.10c: Plots of data on intensity perturbation of the bands of 2,3-diphenylcyclopropenone tetrahydrofuran

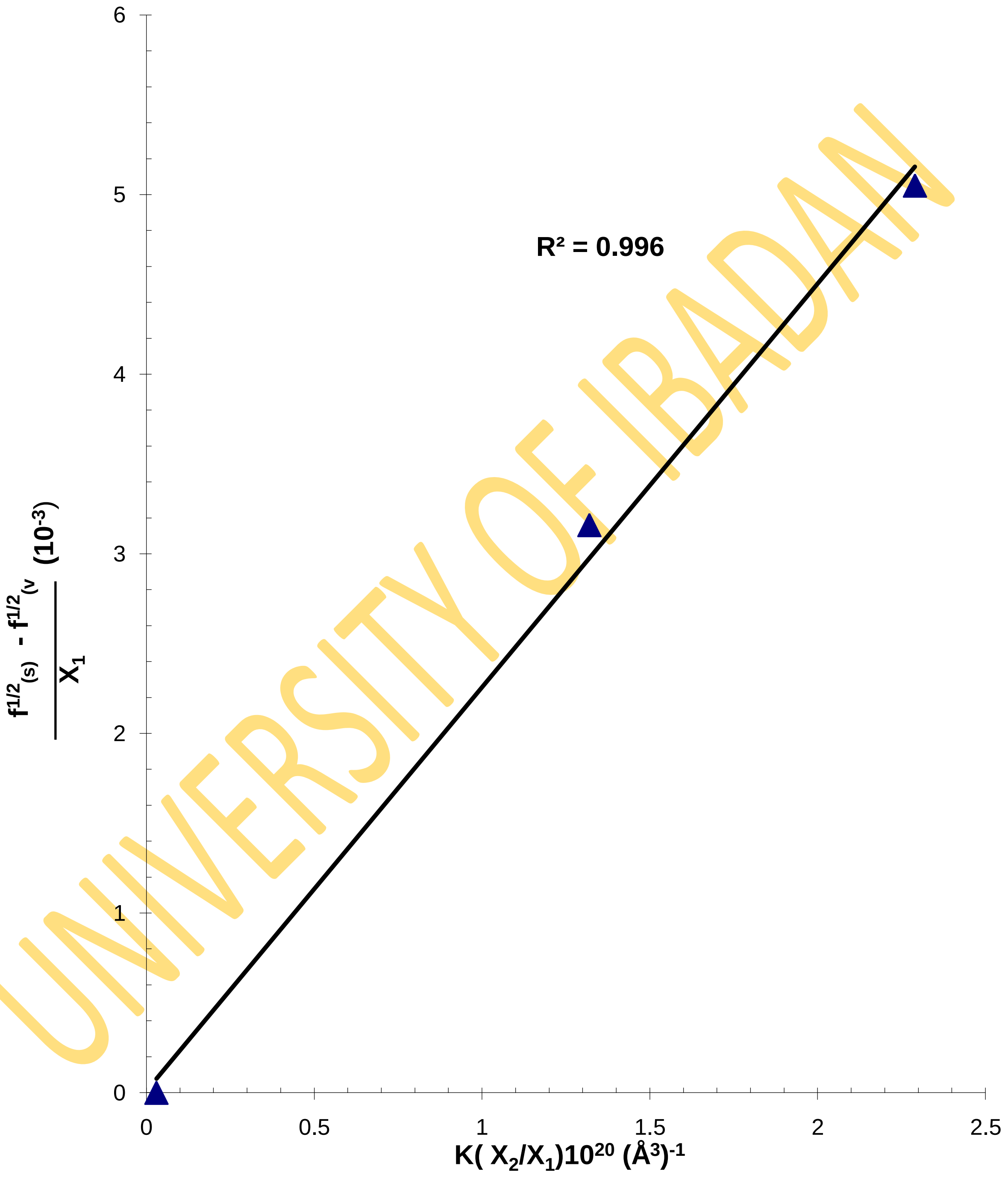


Fig 4.10d: **Plots of data on intensity perturbation of the bands of 2,3-diphenylcyclopropenone in acetonitrile**

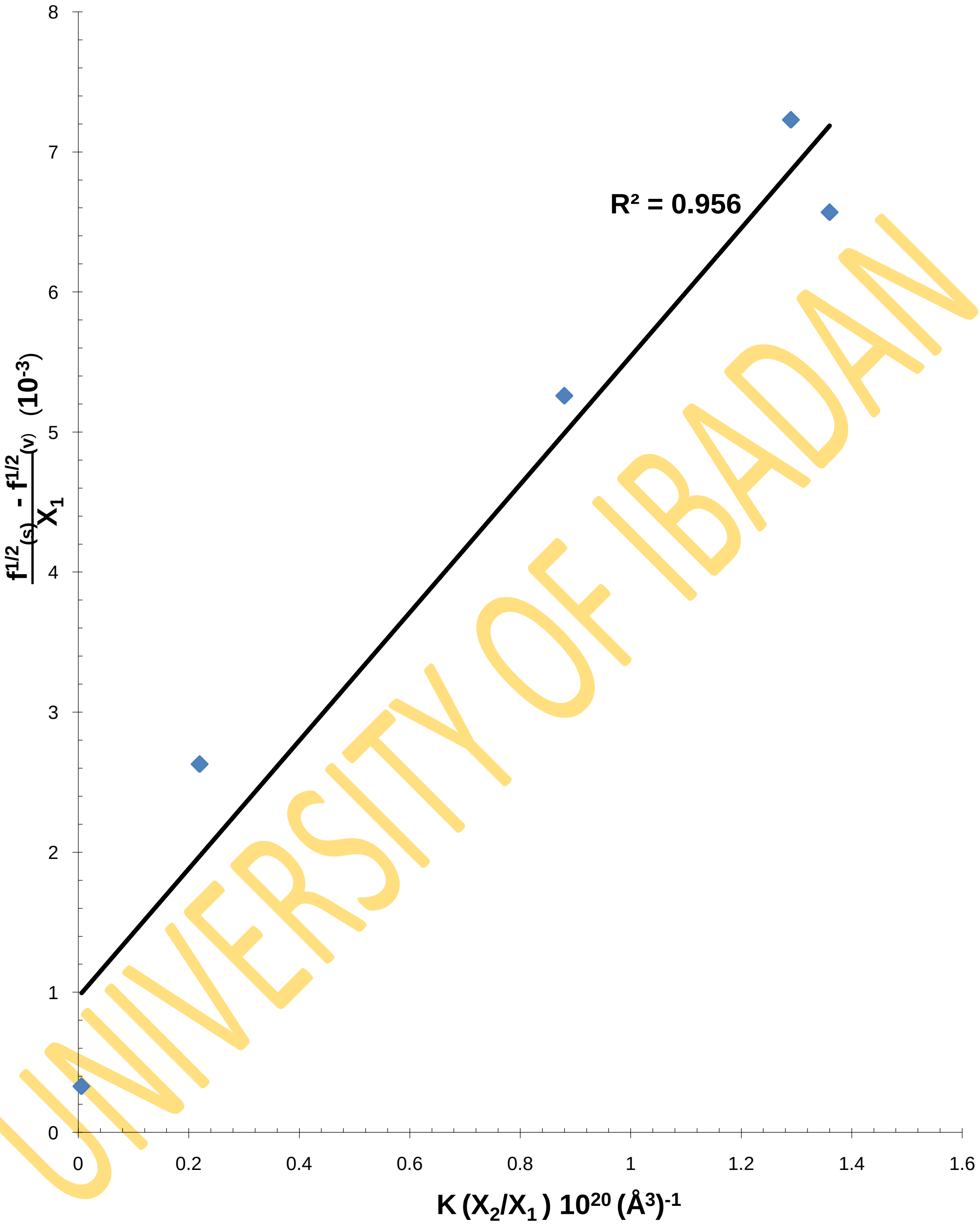


Fig 4.11a: **Plots of data on intensity perturbation of the bands of 9,10-phenanthrenequinone in methanol**

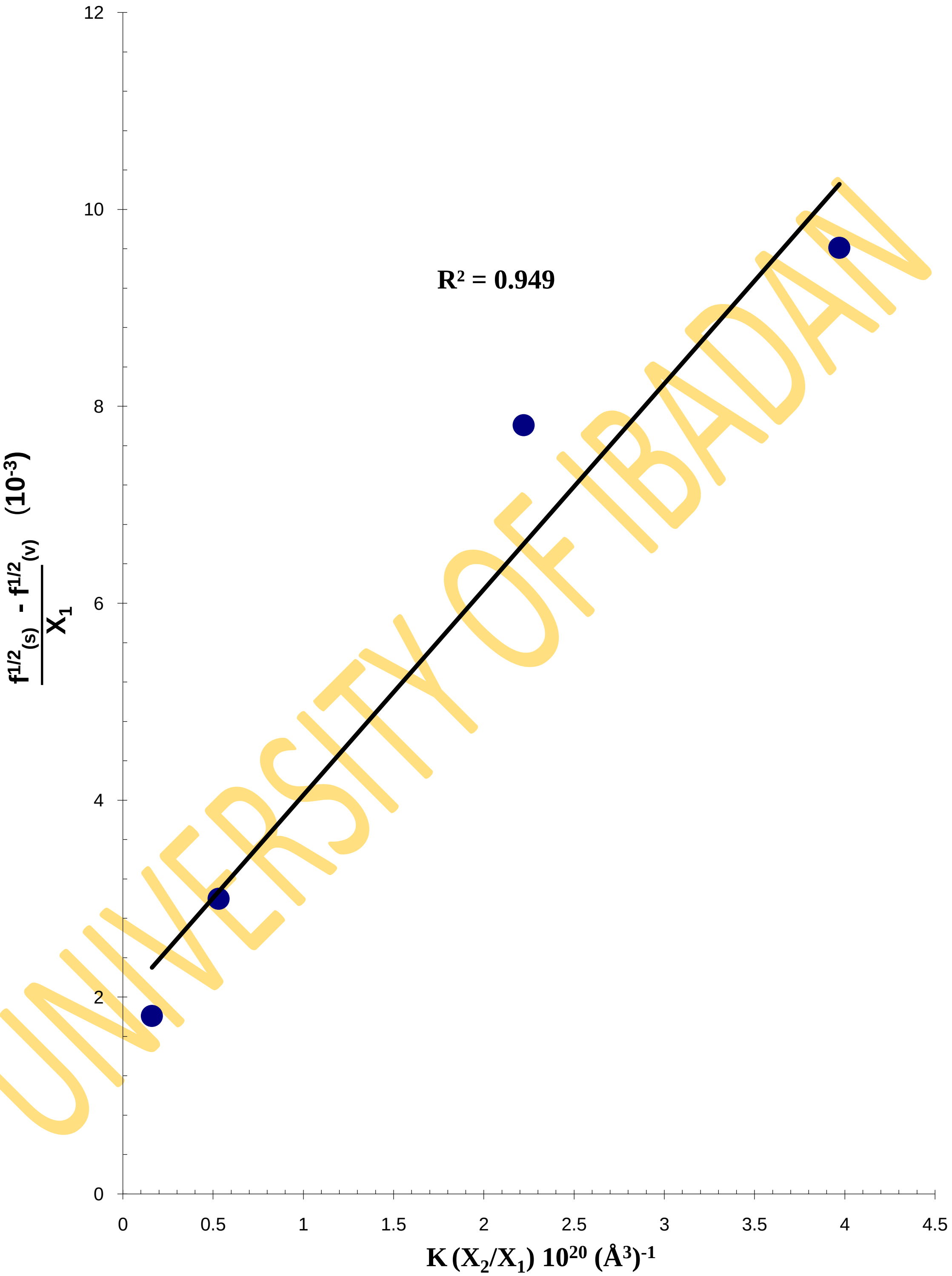


Fig 4.11b: Plots of data on intensity perturbation of the bands of 9,10-phenanthrenequinone in ethanol

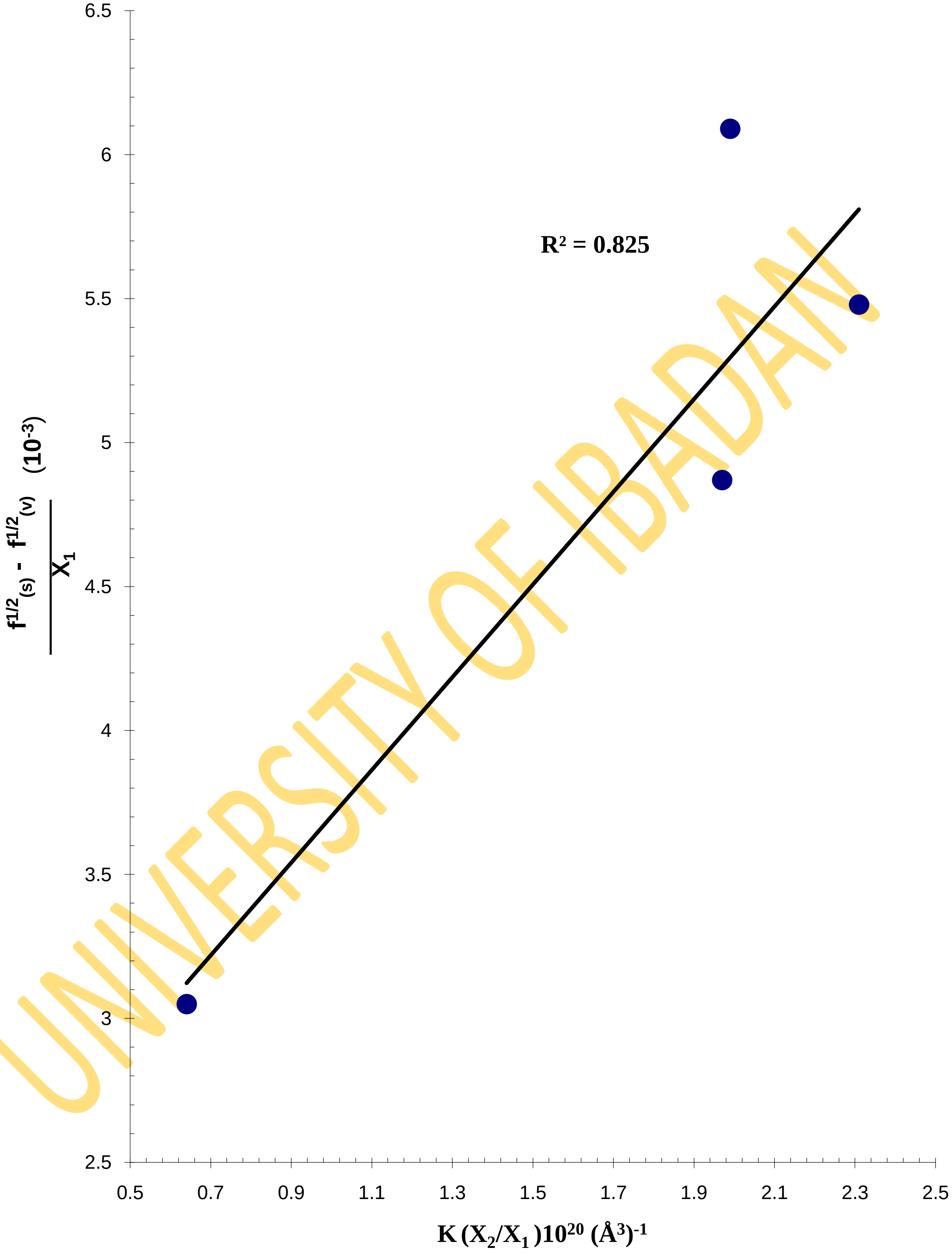


Fig 4.11c: Plots of data on intensity perturbation of the bands of 9,10-phenanthrenequinone in tetrahydrofuran

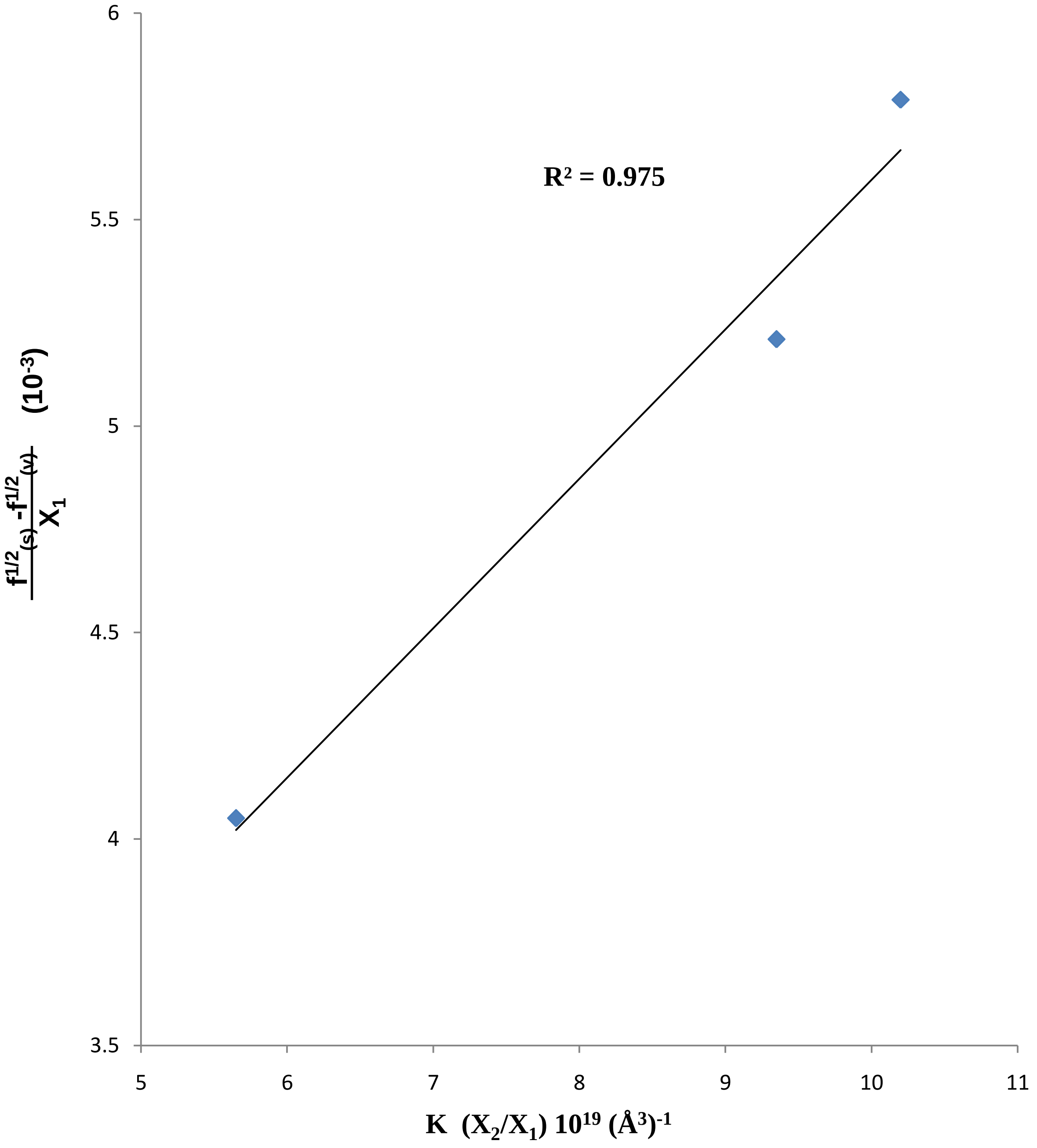


Fig. 4.12a: Plots of data on intensity perturbation of the bands 3,4-diphenylthiophene in methanol

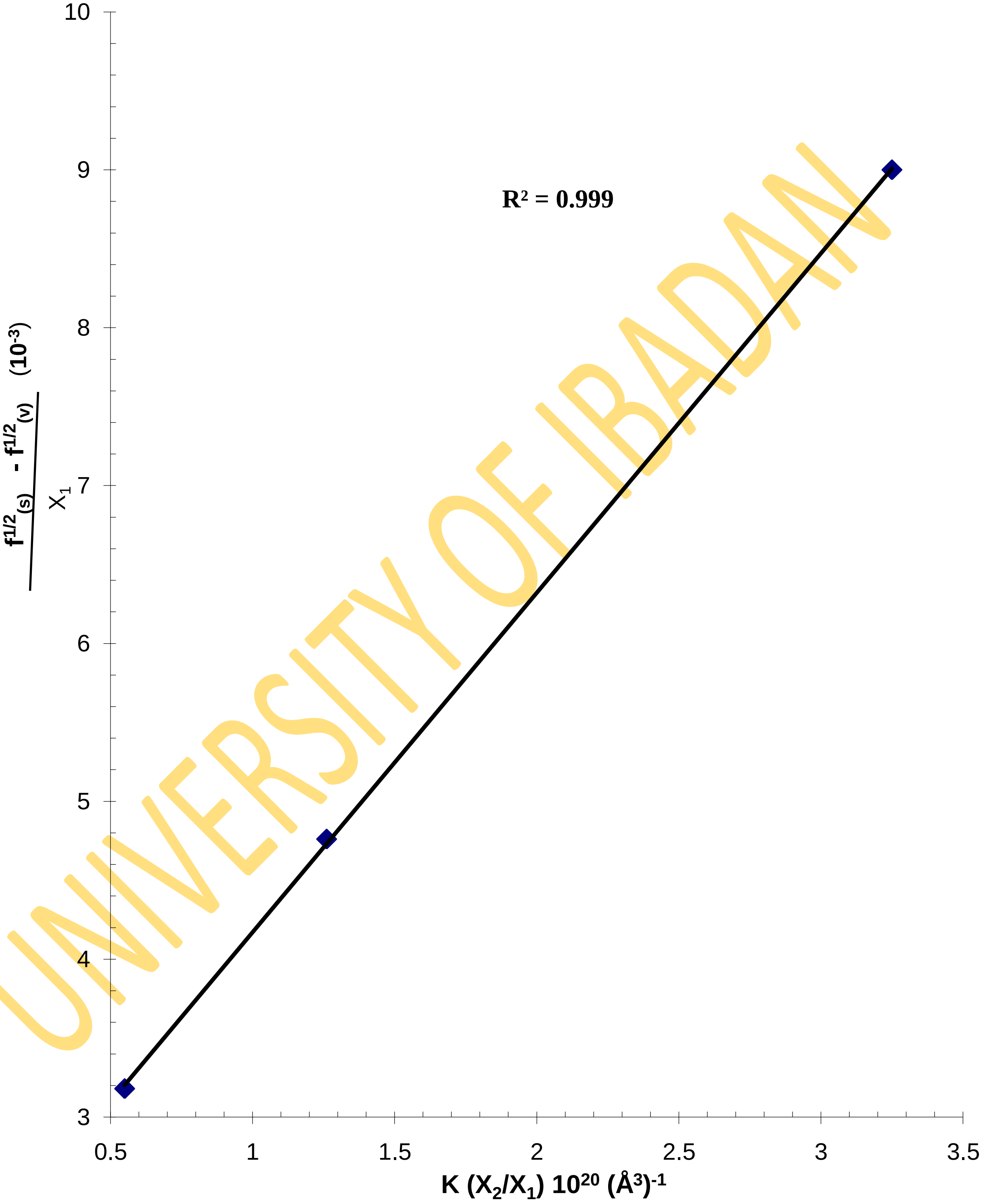


Fig 4.12b: Plots of data on intensity perturbation of the bands of 3,4-diphenylthiophene in ethanol

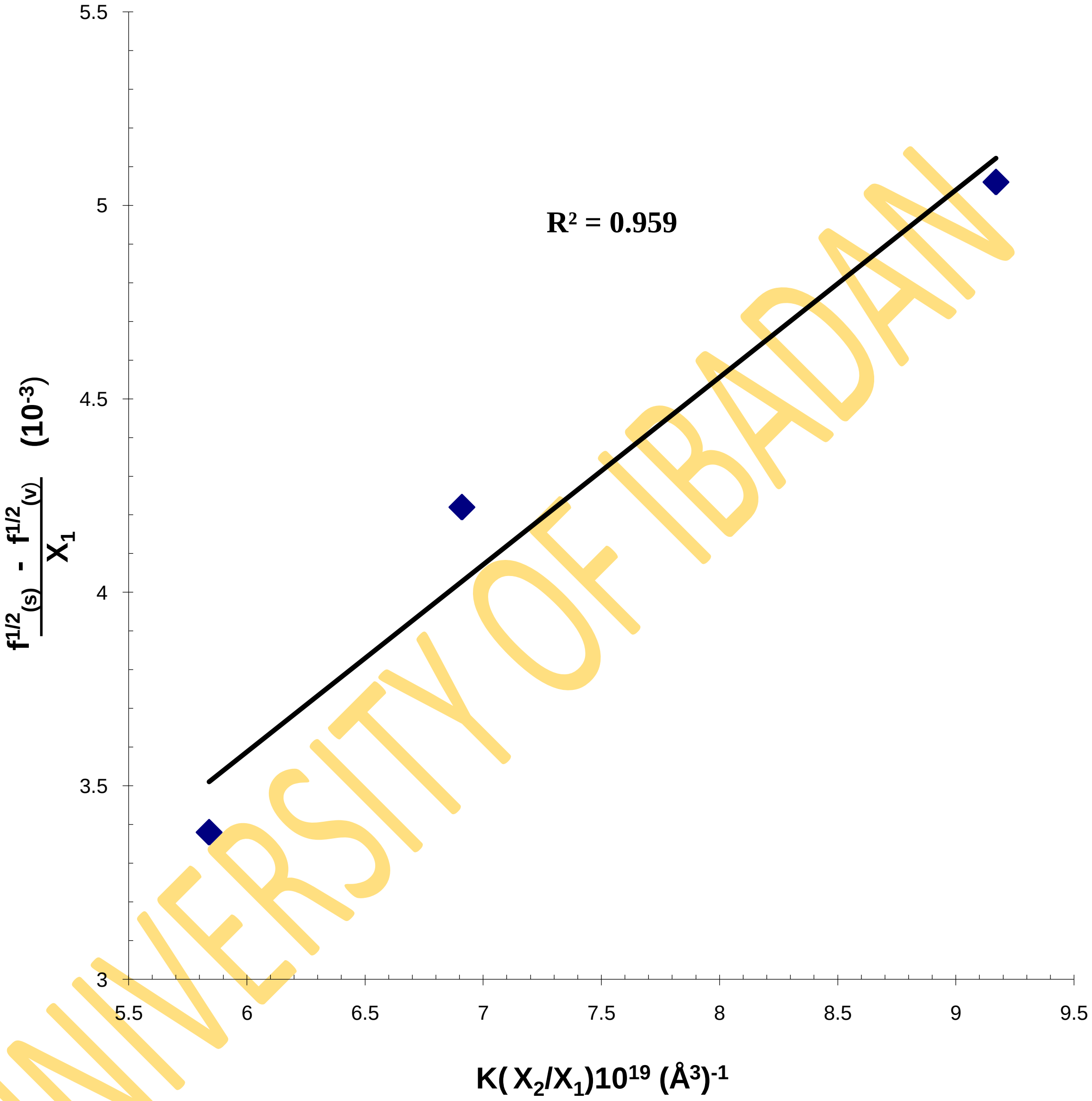


Fig. 4.13a: Plots of data on intensity perturbation of the bands of 3,4- dicarboxylic-2,5-diphenyl thiophene in methanol

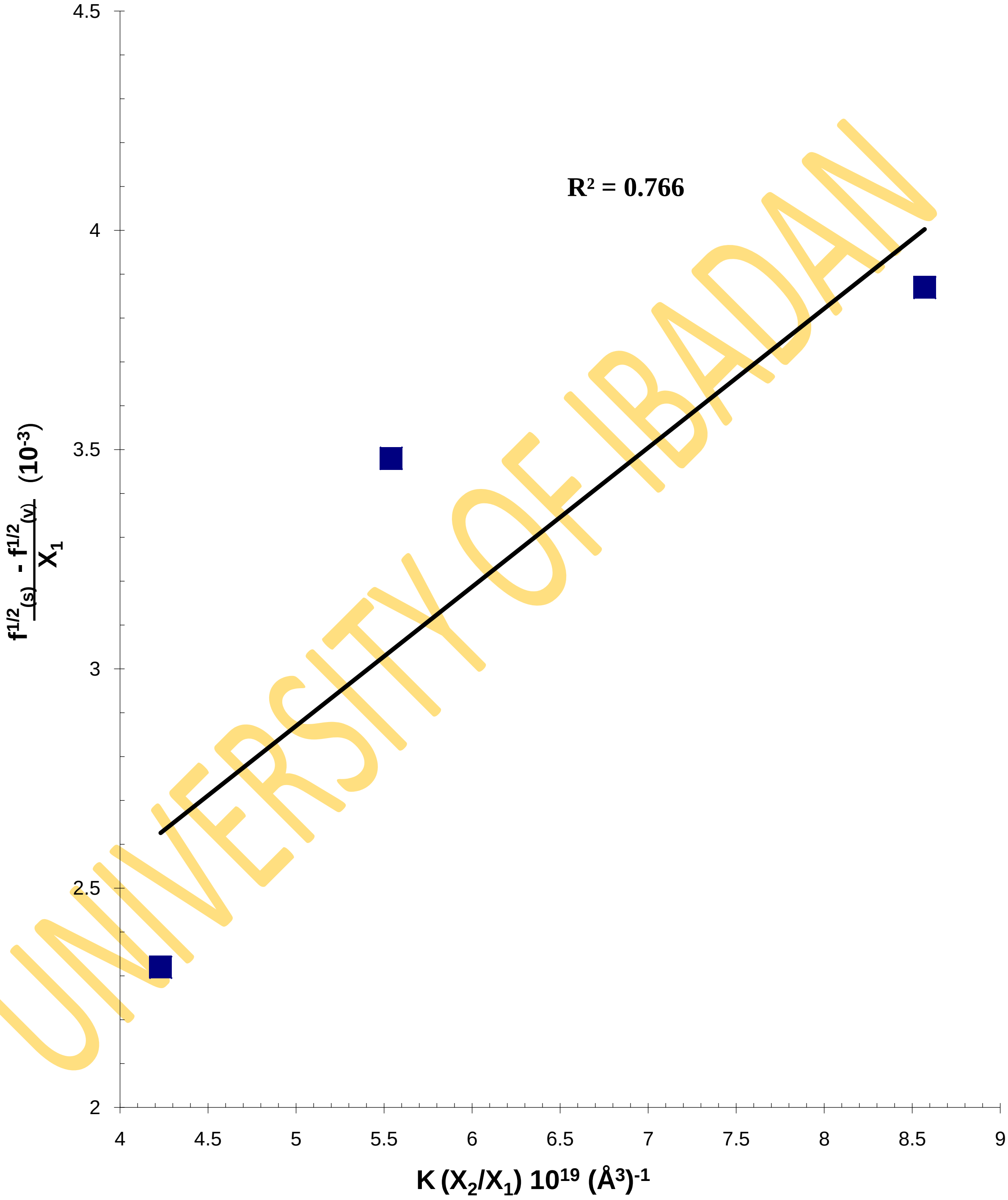


Fig. 4.13b: Plots of data on intensity perturbation of the bands of 3,4-dicarboxylic-2,5-diphenylthiophene in ethanol

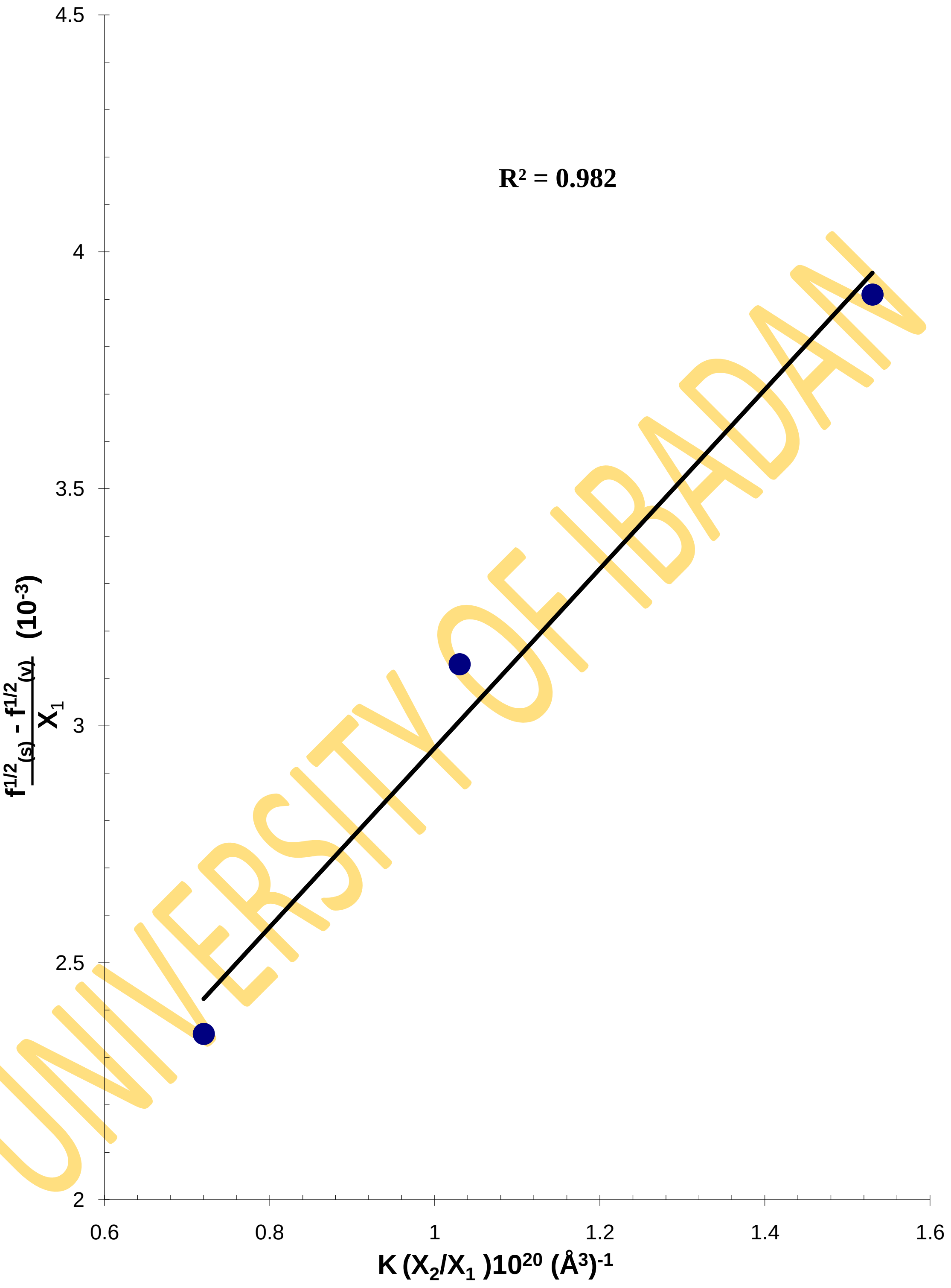


Fig. 4.13c: Plots of data on intensity perturbation of the bands of 3,4-dicarboxylic-2,5-diphenylthiophene in tetrahydrofuran

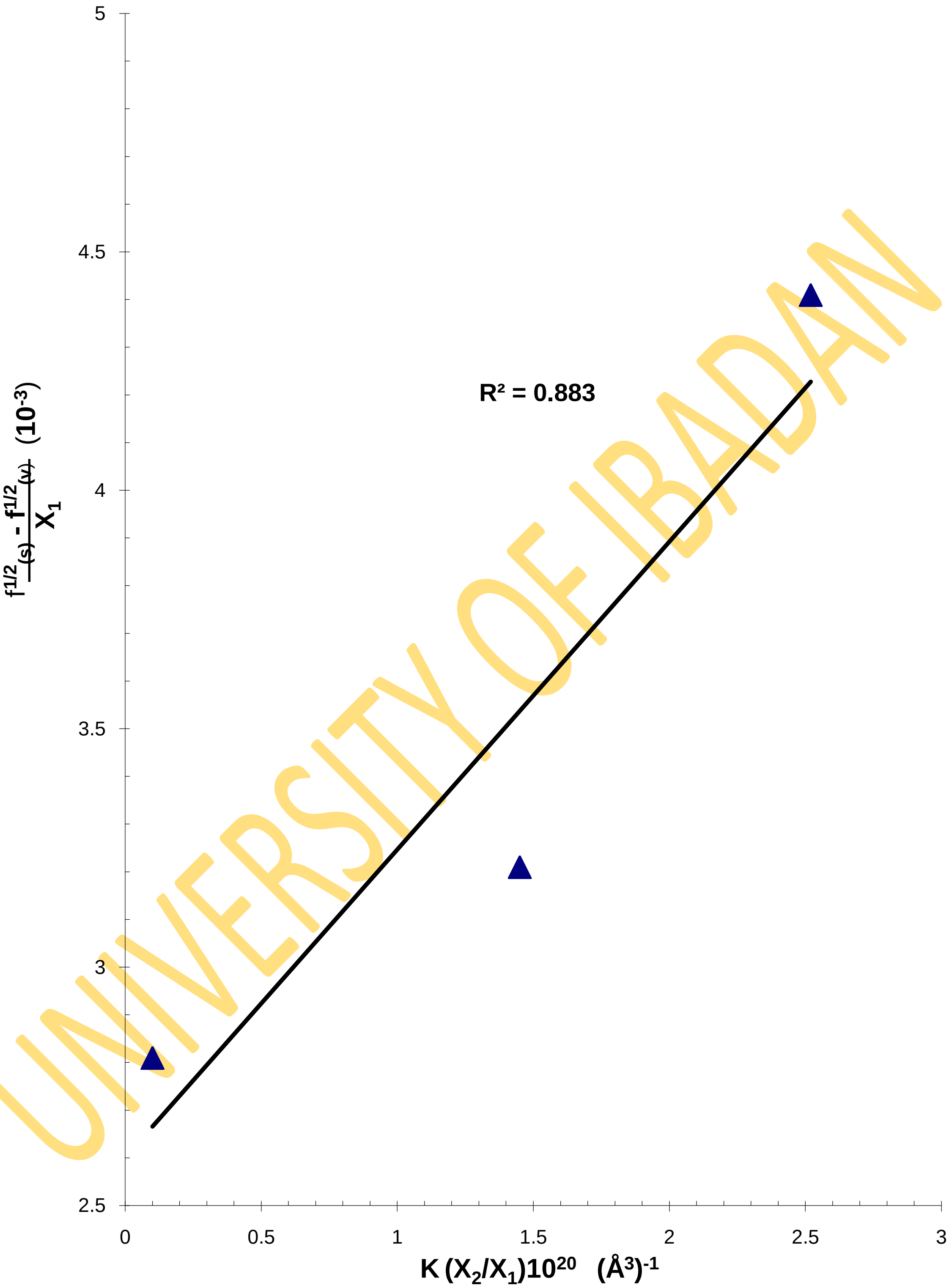


Fig 4.13d: Plots of data on intensity perturbation of the bands of 3,4-dicarboxylic-2,5-diphenylthiophene in acetonitrile

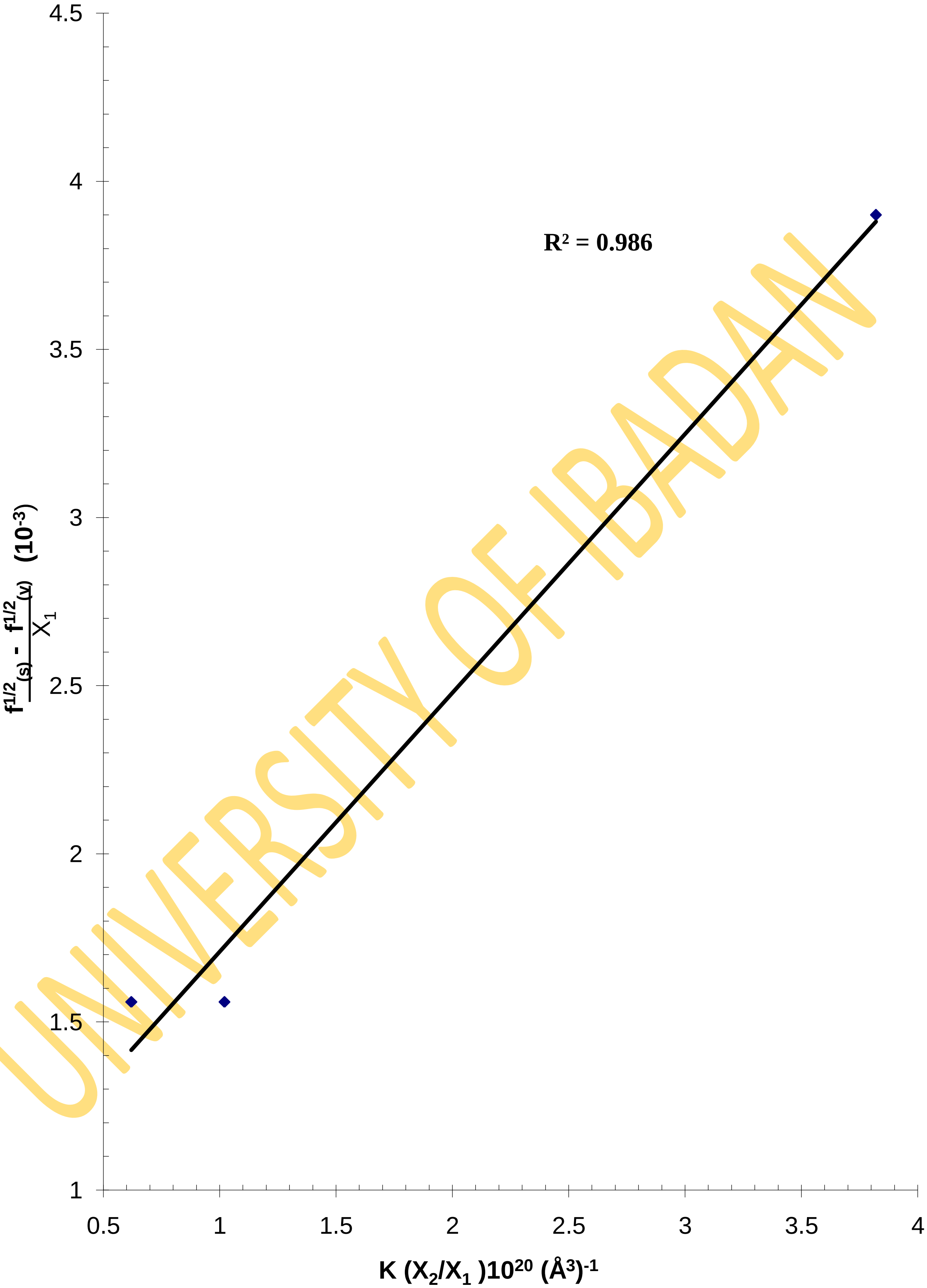


Fig. 4.13e: **Plots of data on intensity perturbation of the bands of 3,4-dicarboxylic-2,5-diphenylthiophene in 1,2-dichloroethane**

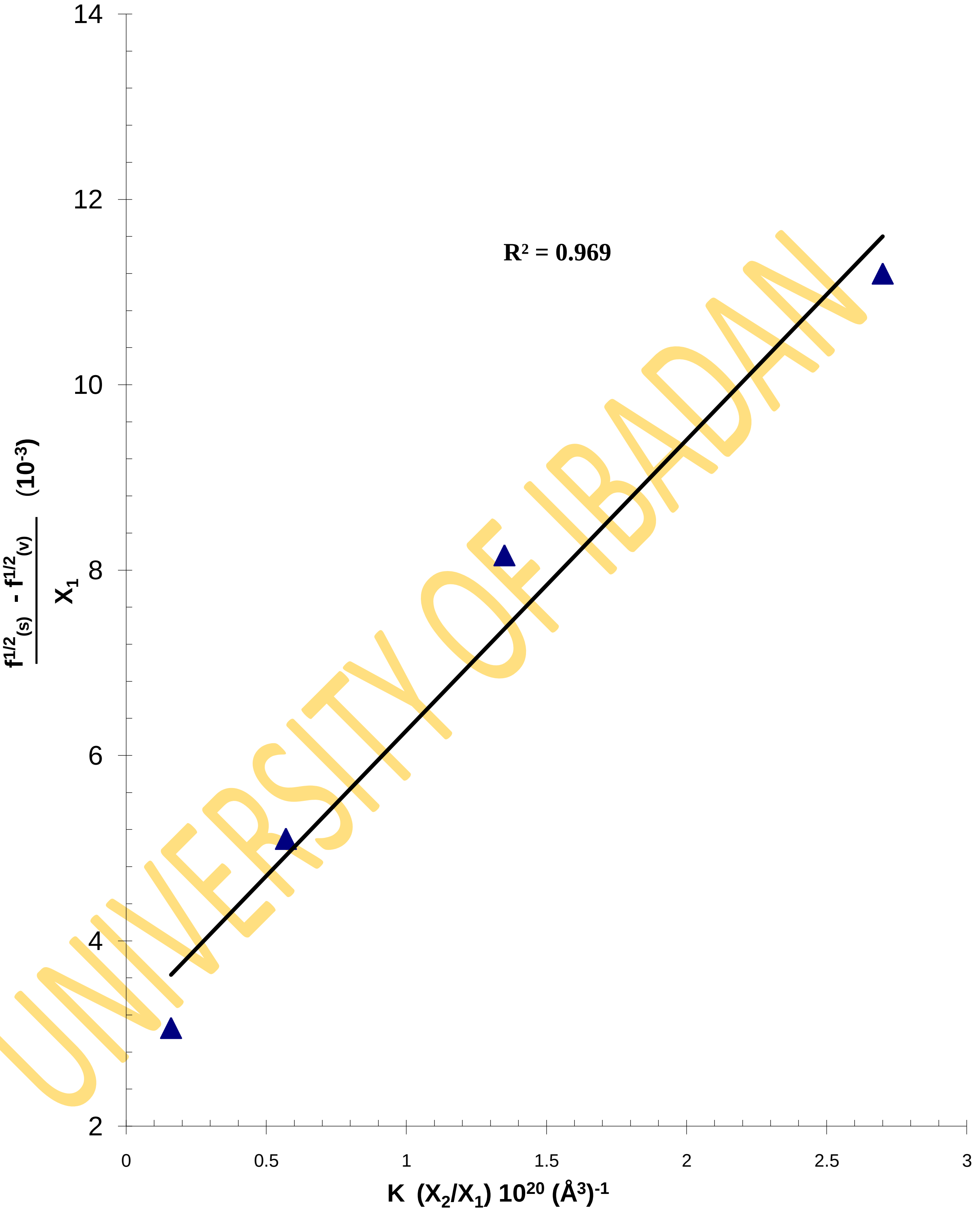


Fig 4.14a: Plots of data on intensity perturbation of the bands benzo[b]thiophene in methanol

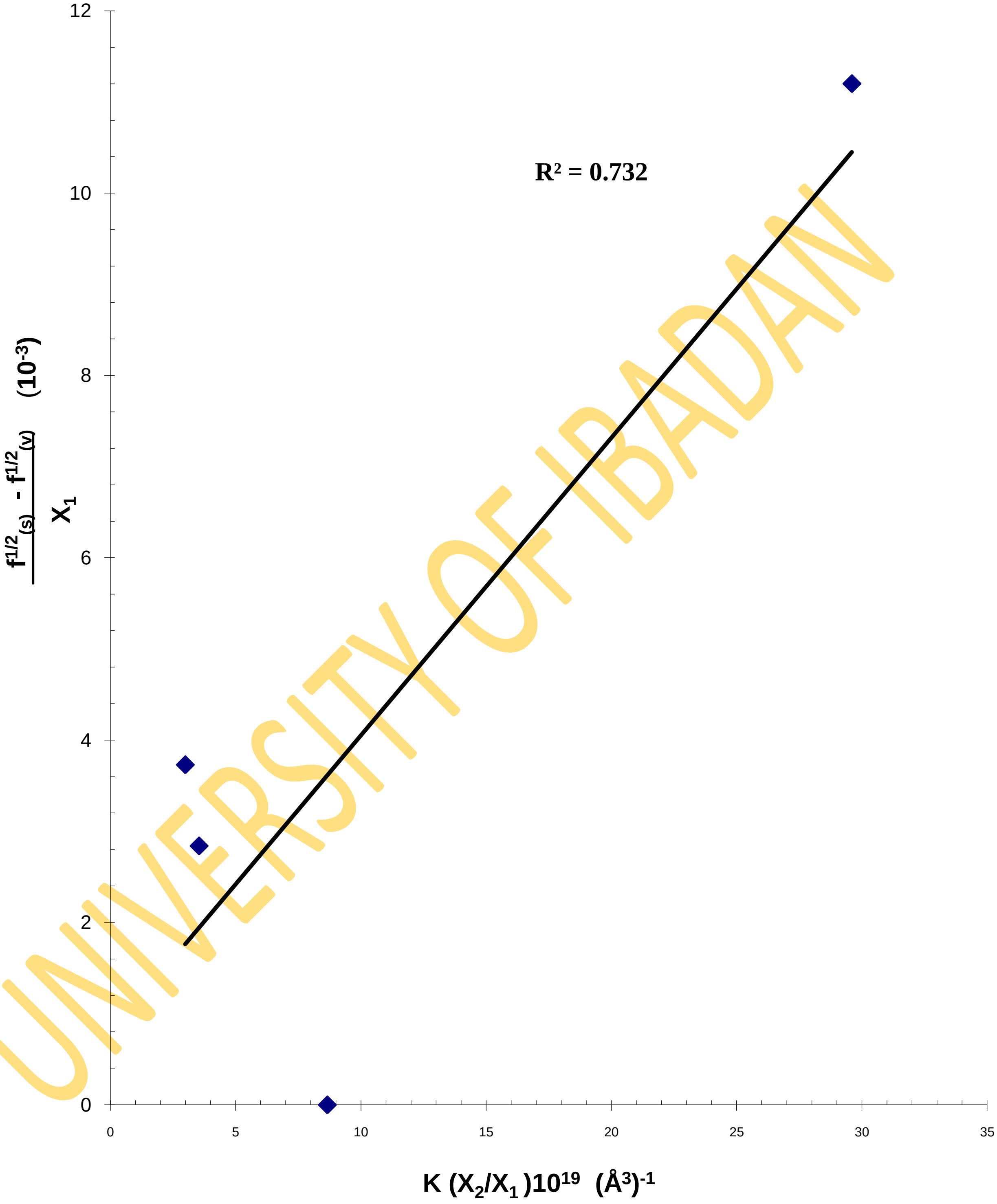


Fig 4.14b: Plots of data on intensity perturbation of the bands benzo[b]thiophene in ethanol

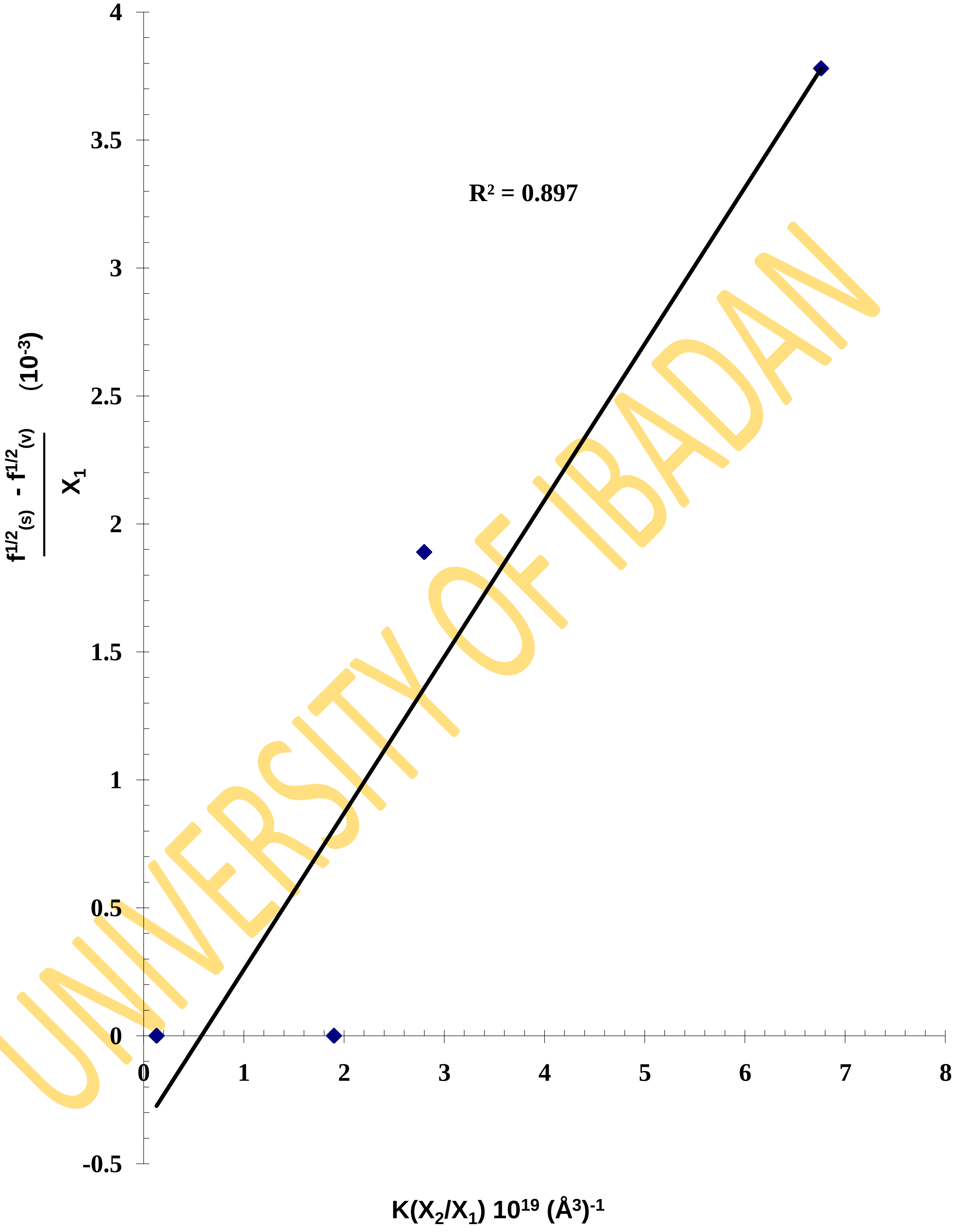


Fig 4.14c: Plots of data on intensity perturbation of the bands benzo[b]thiophene in tetrahydrofuran

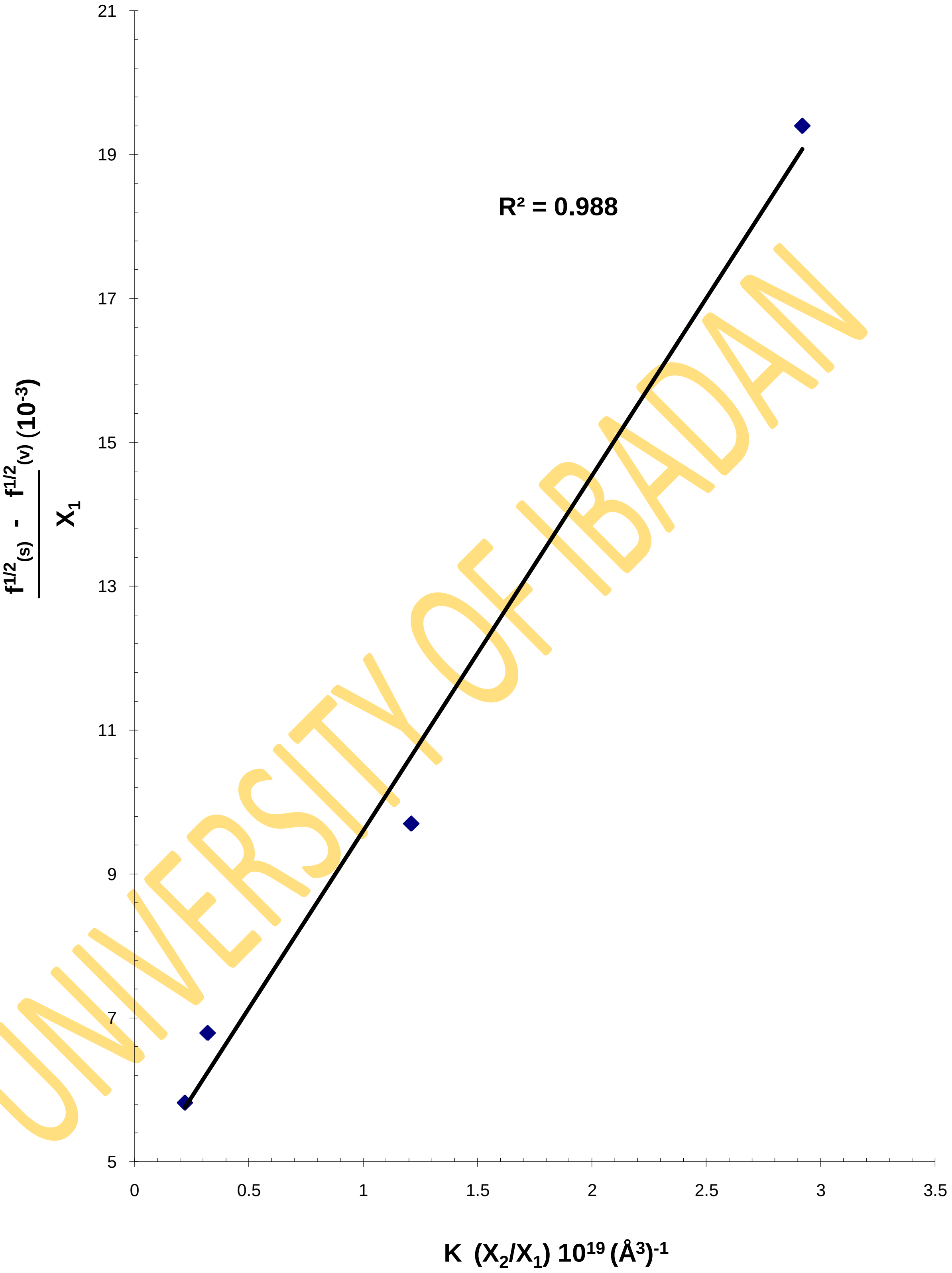


Fig 4.14d: Plots of data on intensity perturbation of the bands benzo[b]thiophene in acetonitrile

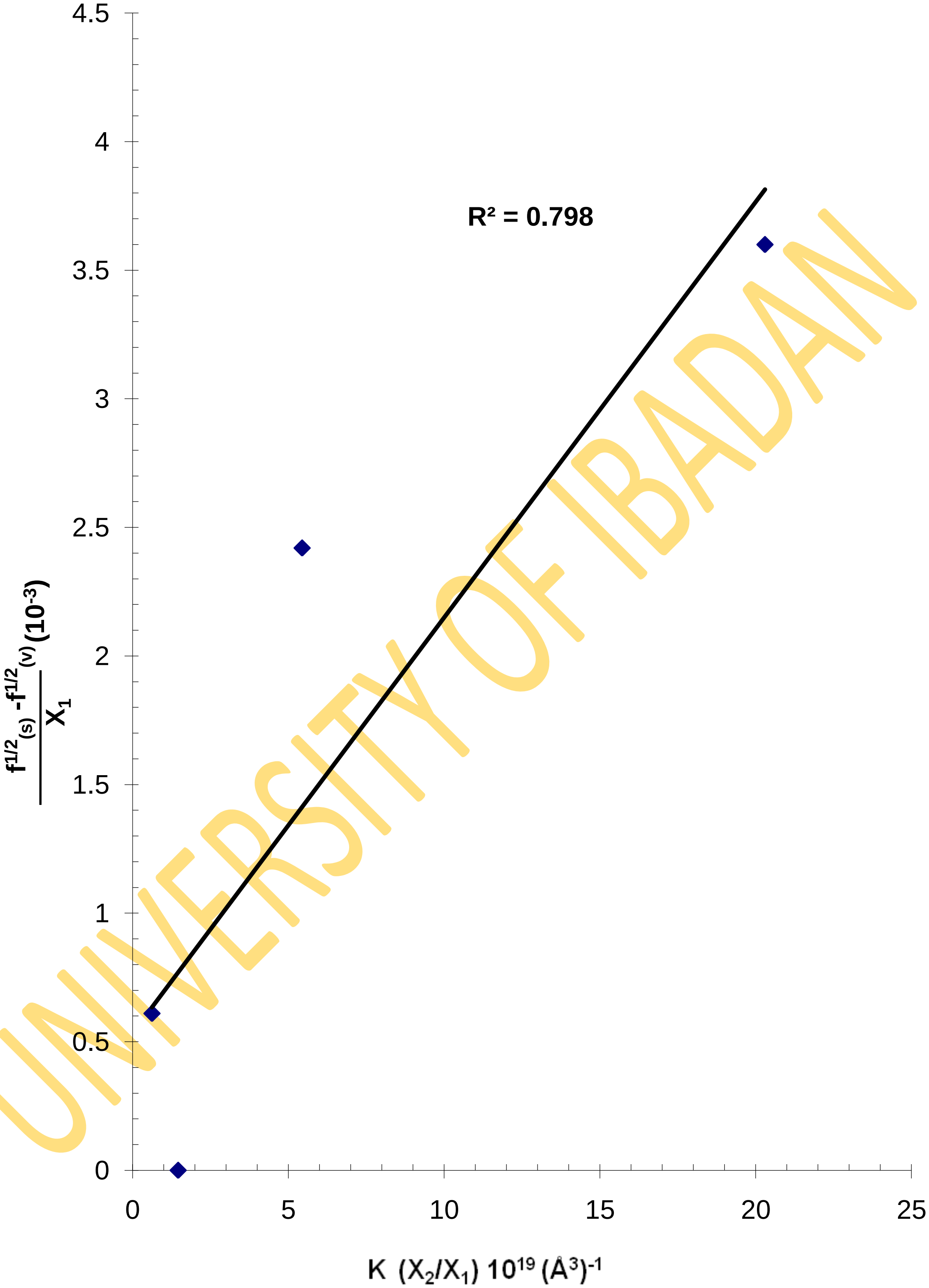


Fig 4.14e: Plots of data on intensity perturbation of the bands benzo[b]thiophene in 1,2-dichloroethane

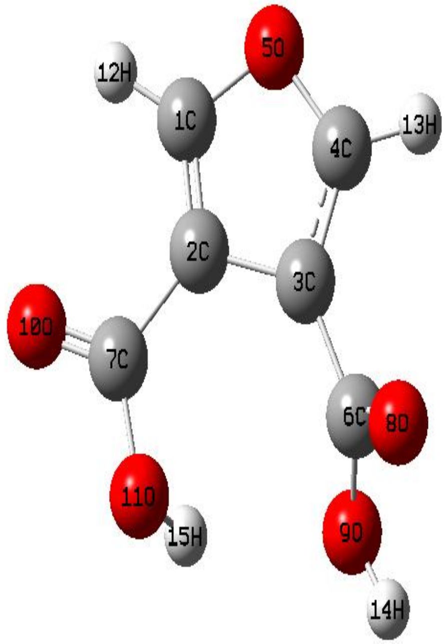


Fig 4.15**:** Optimized structure of furan-3,4-dicarboxylic acid

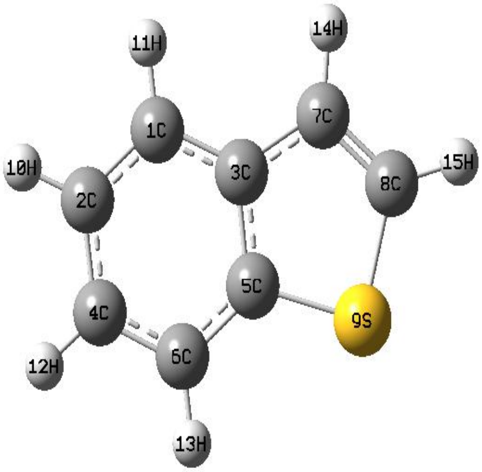


Fig 4.16: Optimized structure of benzo[b]thiophene

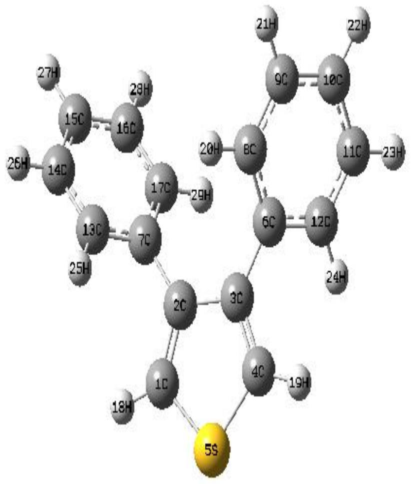


Fig 4.17: Optimized structure of 3,4-diphenylthiophene

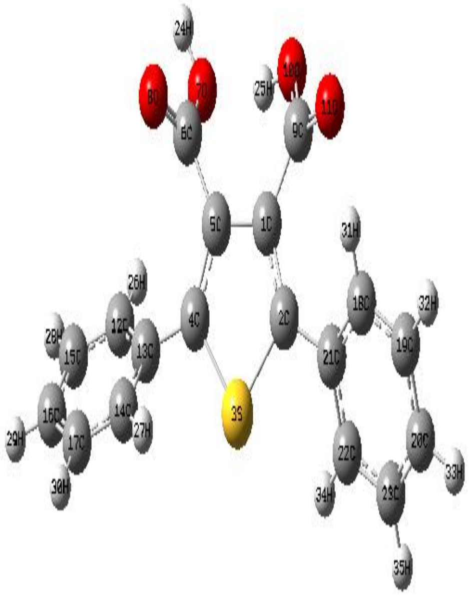


Fig 4.18: Optimized structure of 3,4-dicarboxylic-2,5-diphenylthiophene

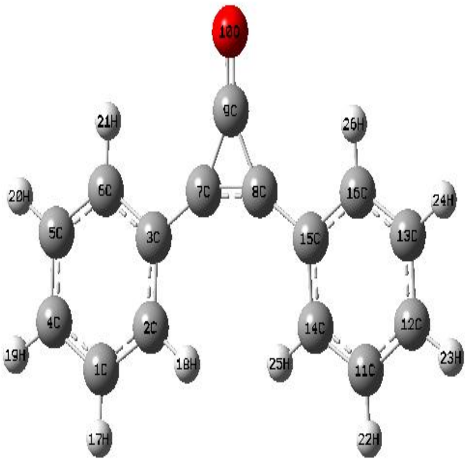


Fig 4.19: Optimized structure of 2,3-diphyenylcyclopropenone

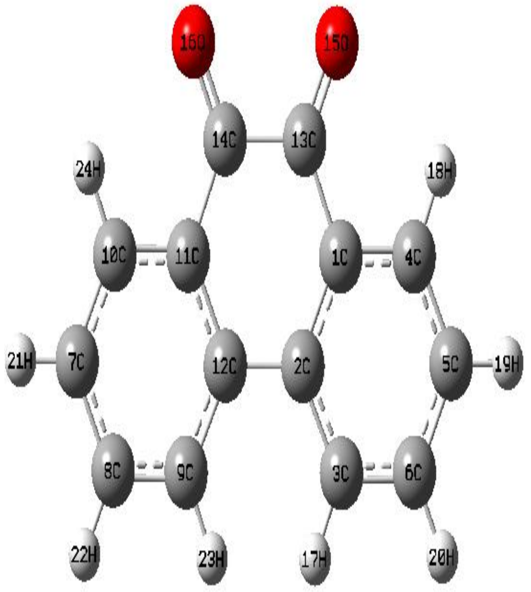


Fig 4.20: Optimized structure of 9,10-phenathrenequinone

Table 4.10: TD-DFT-B3LYP/6-31G* computed singlet state excitations for 2,3-diphenylcyclopropenone

		EXCITED STATES									
Solvent		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Methanol	ν(cm^{-1})	28,267	32,116	36,332	36,409	37,873	41,076	44,024	44,305	44,685	45,078
	f	0.0081	0.8892	0.0222	0.0157	0.0003	0.0003	0.0070	0.0297	0.0016	0.0037
	EE(eV)	3.5047	3.9819	4.5047	4.5140	4.6956	5.0929	5.4583	5.4903	5.5402	5.5889
DCM	ν(cm^{-1})	27682	31,852	36,390	36,471	37,460	41,078	33,436	43,995	44,216	44,555
	f	0.0071	0.9083	0.0230	0.0150	0.0003	0.0002	0.0067	0.0182	0.0022	0.0189
	EE(eV)	3.4321	3.9492	4.5118	4.5218	4.6445	5.0930	5.4123	5.4546	5.4820	5.5242
n-heptanes	ν(cm^{-1})	25,712	31,523	36,054	36,645	36,739	41,088	41,339	41,754	43,636	43,912
	f	0.0038	0.8755	0.0004	0.0189	0.0126	0.0002	0.0012	0.0013	0.0249	0.0424
	EE(eV)	3.1879	3.9083	4.4702	4.5433	4.5550	0.0942	5.1255	5.1757	5.4102	5.4444

f: Oscillator strength, ν : Absorption maximum (in wave number), EE: Excited state energy

Table 4.11: TD-DFT-B3LYP/6-31G* computed singlet state excitations for 9, 10-phenanthrenequinone

		EXCITED STATES									
Solvents		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Methanol	ν(cm^{-1})	18,937	20,250	27,232	27,247	29,420	34,527	39,246	40,167	40,525	41,264
	f	0.000	0.041	0.000	0.049	0.107	0.047	0.127	0.509	0.000	0.0002
	EE(eV)	2.348	2.511	3.376	3.378	3.648	4.281	4.866	4.980	5.025	5.116
DCM	ν(cm^{-1})	18,730	20,585	26,978	27,495	29,590	34,849	39,282	39,994	40,162	40,722
	f	0.000	0.045	0.000	0.050	0.113	0.048	0.134	0.535	0.000	0.0002
	EE(eV)	2.3223	2.5521	3.3449	3.4090	3.6687	4.3207	4.8703	4.9586	4.9795	5.0487
n-heptane	ν (cm^{-1})	18,068	21,890	26,153	28,531	30,451	36,093	38,806	38,861	39,555	
	f	0.0000	0.0492	0.0000	0.0407	0.107	0.0391	0.0002	0.0000	0.1259	
	EE(eV)	2.2402	2.7140	3.2426	3.5374	3.7754	4.4751	4.8113	4.8181	4.9043	

f: Oscillator strength, ν : Absorption maximum (in wave number), EE: Excited state energy

Table 4.12: TD-DFT-B3LYP/6-31G* computed singlet state excitations for benzo[b]thiophene

		EXCITED STATES						
Solvents		**1**	**2**	**3**	**4**	**5**	**6**	**7**
Methanol	ν(cm^{-1})	38,504	41,191	44,506	45,756	48,716	49,142	51,797
	f	0.0955	0.088	0.0001	0.2726	0.0001	0.3006	0.1024
	EE(eV)	4.7739	5.107	5.5179	5.6734	6.040	6.0929	6.4220
DCM	ν(cm^{-1})	38,413	41,102	44,413	45,623	48,629	48,979	51,720
	f	0.1041	0.0919	0.0001	0.2951	0.0001	0.3126	0.1031
	EE(eV)	4.7626	5.096	5.5065	5.6564	6.0291	6.0727	6.4124
n- heptanes	ν(cm^{-1})	38,314	40,963	44,201	45,550	48,450	48,842	51,624
	f	0.0999	0.0806	0.0001	0.3037	0.0001	0.2991	0.1007
	EE(eV)	4.7449	5.0787	5.4801	5.6473	6.0071	6.0557	6.4005

f : Oscillator strength, ν : Absorption maximum (in wave number), EE: Excited state energy

Table 4.13: TD-DFT-B3LYP/6-31G* computed singlet state excitations for 3, 4-diphenylthiophene

		EXCITED STATES									
Solvent		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Methanol	ν(cm^{-1})	38,217	39,725	41,145	41,246	41,925	43,142	43,952	44,543	44,982	44,998
	f	0.1562	0.0013	0.0606	0.0000	0.1127	0.4133	0.0068	0.0091	0.0028	0.0422
	EE(eV)	4.7384	4.9252	5.1014	5.1139	5.1982	5.3489	5.4494	5.5226	5.5771	5.5790
DCM	ν(cm^{-1})	38,158	39,695	41,086	41,234	41,857	43,034	43,937	44,547	44,936	44,960
	f	0.1718	0.0014	0.0709	0.0001	0.1112	0.4341	0.0078	0.0103	0.0020	0.0462
	EE(eV)	4.7309	4.9215	5.0941	5.1124	5.1896	5.3342	5.4473	5.5232	5.5714	5.5743
n-heptane	ν(cm^{-1})	38,153	39,725	40,958	41,215	41,703	42,965	43,900	44,623	44,845	44,859
	f	0.1667	0.0009	0.0838	0.0004	0.0976	0.4278	0.0139	0.0108	0.0026	0.0443
	EE(eV)	4.7304	4.9252	5.0780	5.1100	5.1706	5.3269	5.4430	5.5326	5.5600	5.5618

f : Oscillator strength, ν : Absorption maximum (in wave number), EE: Excited state energy

Table 4.14: TD-DFT-B3LYP/6-31G* computed singlet state excitations for 2, 5-diphenyl-3, 4-dicarboxylicthiophene

		EXCITED STATES									
Solvent		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Methanol	ν(cm^{-1})	30,951	33,618	35,841	36,088	36,316	38,311	39119	39,394	39,928	40,522
	f	0.3246	0.1499	0.0066	0.0190	0.0091	0.0034	0.1576	0.0092	0.0411	0.0922
	EE(eV)	3.8375	4.1680	4.4437	4.4744	4.5027	4.7500	4.8501	4.8830	4.9505	5.0256
DCM	ν(cm^{-1})	30,787	33,629	35,708	35,991	36,311	38,165	39,020	39,316	39,742	40,476
	f	0.3284	0.1666	0.0092	0.0213	0.0097	0.0092	0.1551	0.0054	0.0387	0.1078
	EE(eV)	3.8171	4.1695	4.4273	4.4623	4.5019	4.7319	4.8378	4.8745	4.9275	5.0185
n- heptanes	ν(cm^{-1})	30,540	33,882	35,399	35,885	36,649	37,636	38,662	39,279	39,524	40,269
	f	0.2958	0.1773	0.0254	0.0333	0.0089	0.0348	0.0938	0.0328	0.0090	0.0800
	EE(eV)	3.7865	4.2009	4.3890	4.4492	4.5440	4.6663	4.7935	4.8700	4.9004	4.9927

f: Oscillator strength, ν : Absorption maximum (in wave number), EE: Excited state energy

Table 4.15: TD-DFT-B3LYP/6-31G* computed singlet state excitations for Furan-3, 4-dicarboxylic acid

		EXCITED STATES									
Solvents		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Methanol	ν(cm^{-1})	38,385	39,623	41,372	43,195	45,263	47,295	49,099	51,013		
	f	0.0034	0.0682	0.0012	0.0028	0.0118	0.1289	0.0771	0.0052		
	EE(eV)	4.7591	4.9125	5.1294	5.3556	5.6119	5.8637	6.0876	6.3248		
DCM	ν(cm^{-1})	37,809	39,442	40,890	42,294	45,562	46,633	48,821	50,950	52,433	
	f	0.0021	0.0673	0.0017	0.0028	0.0121	0.0870	0.1388	0.0053	0.0770	
	EE(eV)	4.6876	4.8901	5.0696	5.2438	5.6491	5.7818	6.0531	6.3169	6.5009	
n-heptane	ν(cm^{-1})	35,458	38,346	38,933	39,923	43,562	46,624	49,039	50,505	50,728	
	f	0.0005	0.0069	0.0442	0.0017	0.0341	0.0072	0.2114	0.0050	0.0051	
	EE(eV)	4.3962	4.7543	4.8271	4.9498	5.4010	5.7807	6.0799	6.2619	6.2893	

f: Oscillator strength, ν : Absorption maximum (in wave number), EE: Excited state energy

Table 4.16: Theoretically computed transition dipole moment (D) of the compounds

	TRANSITION STATES									
Solvents	1	2	3	4	5	6	7	8	9	10
					Benzo[b]thiophene					
Methanol	0.903	0.839	0.0203	1.400	0.023	1.419	0.801			
DCM	0.945	0.858	0.020	1.459	0.024	1.449	0.807			
n-heptane	0.927	0.805	0.199	1.482	0.025	1.419	0.810			
					3,4-diphenylthiophene					
Methanol	1.156	0.102	0.696	0.015	0.941	1.776	0.225	0.260	0.141	0.556
DCM	1.194	0.107	0.754	0.024	0.935	1.810	0.241	0.276	0.122	0.570
n-heptane	1.218	0.086	0.821	0.058	0.878	1.823	0.323	0.283	0.138	0.582
					2,5-diphenyl-3,4-dicarboxylicthiophene					
Methanol	1.786	1.211	0.292	0.417	0.287	0.172	1.152	0.213	0.582	0.936
DCM	1.858	1.277	0.246	0.441	0.297	0.281	1.143	0.278	0.566	0.866
n-heptane	1.874	1.313	0.888	0.553	0.282	0.552	0.894	0.524	0.275	0.809

Table 4.16 (Continued): Theoretically computed transition dipole moment (D) of the compounds

	TRANSITION STATES									
Solvents	1	2	3	4	5	6	7	8	9	10
Furan-3,4-dicarboxylic acid										
Methanol	0.170	0.753	0.098	0.145	0.293	0.947	0.719	0.183		
DCM	0.136	0.750	0.115	0.147	0.300	0.784	0.967	0.185		
n-heptane	0.070	0.243	0.611	0.119	0.508	0.226	1.191	0.181		
2,3-diphenylcyclopropenone										
Methanol	0.306	3.019	0.449	0.377	0.050	0.049	0.228	0.470	0.110	0.164
DCM	0.291	3.064	0.458	0.368	0.050	0.042	0.225	0.370	0.128	0.374
n-heptane	0.220	3.024	0.062	0.412	0.336	0.361	0.981	0.445	0.434	0.564
9,10-phenathenequinone										
Methanol	1.160	0.102	0.696	0.015	0.941	1.776	0.225	2.098	0.142	0.556
DCM	0.007	0.846	0.0003	0.771	1.123	0.675	1.058	0.260	0.0001	0.040
n-heptane	0.006	0.860	0.0001	0.685	1.076	0.597	0.038	0.0001	1.024	2.079

Table 4.17 (Continued): HOMO, LUMO, energy gaps (LUMO - HOMO) and related molecular properties of the compounds

Solvents	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{(LUMO-HOMO)}$ (eV)	χ (eV)	ω (eV)	IP (eV)	EA (eV)	η (eV)	S (eV)	μ (D)	α ($Å^3$)
3,4 dicarboxylic-2,5 diphenyl thiophene											
Methanol	-6.321	-1.922	4.399	-4.122	3.862	6.321	1.922	2.200	0.227	5.651	130.10
DCM	-6.324	-1.935	4.389	-4.130	3.885	6.324	1.935	2.195	0.228	6.378	130.40
n-heptane	-6..332	-1.974	4.358	-4.153	3.958	6.332	1.974	2.179	0.230	6.594	131.36
Furan-3, 4- dicarboxylic acid											
Methanol	-7.513	-2.082	5.431	-4.798	4.238	7.513	2.082	0.1841	4.798	9.878	66.21
DCM	-7.580	-2.157	5.423	-4.869	4.371	7.580	2.157	0.1844	4.869	9.547	66.16
n-heptane	-7.512	-2.081	5.431	-4.797	4.236	7.512	2.081	0.1841	4.797	8.377	66.05

Table 4.17 (Continued.): HOMO, LUMO, energy gaps (LUMO-HOMO) and related molecular properties of the compounds

Solvents	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{(LUMO-HOMO)}$ (eV)	χ (eV)	ω (eV)	IP (eV)	EA (eV)	η (eV)	S (eV)	μ (D)	α (Å^3)
2, 3-diphenylcyclopropenone											
Methanol	-6.323	-2.022	4.301	-4.173	4.048	6.323	2.022	2.151	0.232	6.031	85.640
DCM	-6.305	-2.024	4.281	-4.165	4.051	6.305	2.024	2.141	0.234	7.033	85.890
n-heptane	-6.142	-2.043	4.099	-4.093	4.088	6.142	2.043	2.049	0.244	7.335	86.881
9,10-phenanthraquinone											
Methanol	-6.54	-3.36	3.190	-4.950	7.705	6.540	3.361	1.592	0.314	9.471	158.23
DCM	-6.56	-3.33	3.230	-4.950	7.609	6.560	3.330	1.610	0.311	9.032	157.46
n-heptane	-6.64	-3.26	3.380	-4.950	7.249	6.640	3.260	1.690	0.296	7.590	88.45

CHAPTER FIVE

DISCUSSION

The discussion on the molecular orbital calculations on the studied compounds is subdivided into the following:

i. Effect of solvent on the band systems and relative transition energies of the compounds
ii. Oscillator strength and solvent effect
iii. Substituents effect
iv. Transition dipole moments and transition polarizabilities.
v. LUMO - HOMO energy gaps and related molecular properties.

5.1 Effect of solvent on the band system and relative transition energies 3,4-diphenylcyclopropenone

The representative electronic absorption spectra of DPCP showing the effects of solvent on its spectral properties, the summarized data of the transition frequencies (energies) and the corresponding molar absorptivities of this compound in different solvents are presented in Tables 4.1 and Figure 4.1.

Two to four bands were observed in the UV region of the spectra depending on the solvents polarity. In the polar and non polar solvents (except in ethanol, dichloromethane and dichloroethane), three prominent bands were observed. In increasing order of transition energies, Band I ($S_o \rightarrow S_1$), a low intensity shoulder around 32,051-28,986 cm^{-1} in tetrahydrofuran ($\varepsilon_{(v_{\max})}$ = 1,428), dichloromethane ($\varepsilon_{(v_{\max})}$ = 4,814) and 1,2-dichloroethane ($\varepsilon_{(v_{\max})}$ = 5,860) is absent in the spectrum of the compound in the other solvent. This band is both quantum-mechanically and overlap forbidden as reflected by its low intensity. It is slightly shifted to a longer wavelength with increasing solvent polarity showing that the first singlet state of the compound is a π-π* transition. Red shifts were also observed for bands II, III and IV in these solvents.

Band II ($S_o \rightarrow S_1$) is more sensitive to solvent perturbation than band I. It increased intensity (as indicated by the $\varepsilon_{(\nu_{\max})}$ values) shows that the transition is quantum mechanically allowed but overlap forbidden (Bayliss, 1969; Atkins and De-Paula, 2006). The absence of the n-π^* in the spectrum of this molecule can be presumably ascribed to it being hiding under the envelope of strong charge transfer (CT) character of the excited state of this molecule (Amrallah *et al*., 2005). The appearance of two or three bands for the spectrum of this compound in most solvents used is due to the mixing of its excited state, which is manifested by the overlap of some of the bands (Munish *et al*., 2004).

Diffused vibrational structures which manifest itself in the spectral of the DPCP in cyclohexane, heptane, and in the band III of this compound in dichloromethane show that the compound is a rigid molecule in these solvents. On the other hand, the spectrum of diphenylcyclopropenone in methanol and other polar solvents do not show any diffused vibrational fine structure, showing that there is high interaction of this molecule with polar solvent. This may be due to dipole-dipole interactions (Munish, 2004). The intensities of absorption as indicated by the calculated molar absorptivities values shown in Table 4.1 allows band 1 to be assigned $^1A \rightarrow {}^1L_a$, band II as $^1A \rightarrow {}^1L_b$, band III as $^1A \rightarrow {}^1B_b$ while band IV is assigned $^1A \rightarrow {}^1B_a$ transitions (Platts, 1951 and 1953; Iweibo *et al*.,1982; Amrallah *et al*.,2005).

From the computational results in Table 4.11, ten singlets excited states were recorded on the UV-absorption spectra of this molecule as opposed to two or three bands observed in the experimental result. These show that, computationally, the extent of overlap of the transition bands is low. Hypsochromic shifts were observed for virtually all the transitions except the excited states 4 and 6 which are slightly shifted towards the red region of the spectra in polar solvent. Associated with the red shift is the decrease in absorption intensity in both polar and non polar solvents. For the excited states that are shifted towards the blue region of the spectrum, there are increase in excitation energy, showing that the ground states of this molecule at this region is more solvated and more polar than its corresponding excited states. This is also supported by the experimental results.

9, 10-phenanthrenequinone

Two to five bands were observed from the spectra and the summarized spectral properties of this compound as shown in Figure 4.2 and Tables 4.1 respectively. These are in the frequencies range of 49,505-23,810 cm^{-1} depending on solvent polarity. These bands can be designated as $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$, $S_0 \rightarrow S_4$ and $S_0 \rightarrow S_5$ in the order of increasing energies. The two electronic absorption bands located in the regions 47,170-45,045 and 38,910 - 38760 cm^{-1} can be attributed to be the specific bands for the localization of π electrons in benzene rings of the molecules (Amrallah *et al.*, 2005). The red shift as the dielectric constant of the solvent increases in addition to their high molar absorptivities substantiate their π -π* nature (Raikal *et al.*, 2010; Praveen *et al.*, 2011).

In polar solvents such as methanol, ethanol, tetrahydrofuran and acetonitrile, five bands were observed, showing that these solvents are highly transparent to the exciting light in the ultra-violet region of the spectrum of the compound. Although, bands III and IV are not well separated but almost fused to each other in ethanol, methanol and tetrahydrofuran (THF). In the chloro-substituted solvents (dichloromethane and 1,2-dichloroethane), two to four bands were observed owing to different degree of overlap of some of the bands and as a result of the mixing of their excited states (Obi-Egbedi *et al.*, 1998).

This can be justified by the spectrum of the compound in figure 4.2 where band IV appears as shoulder in band III. The observed vibrational fine structures of band II of the compound in non polar solvents indicate that its interaction with these solvent is very weak. The high molar absorptivity despite the blue shifts observed for band III of this compound in polar solvent suggests a mechanism involving molecular orientation of the dicarbonyl substituted compounds and the possibility of 2(n-π*) transition due to two carbonyl groups adjacent to each other. Band IV is also a very intense transition, indicating it quantum-mechanical and overlap allowance (Obi-Egbedi *et al.*, 1998). It is red shifted in polar solvent, depicting that the excited state of this transition is more charged (more solvated and stabilized) than the ground state (Reichardt, 1998). This is also observed for band V, although, not as intense as transitions in bands III and IV. In general, for all cases of the five bands, there exist both blue and red shift with very highmolar absorptivities.

This suggests the posibility of both n-π* and π-π* transitions and high delocalzation of electrons by the UV-absorption of this molecule (Munish *et al*., 2004; Kalsi, 2005).

The computational results (Table 4.10) recorded ten excited states for this compound in the UV-region, an indication of lesser overlapping of the transition bands (Munish *et al*., 2004). Bathochromic shift (associated with π-π*) in polar solvent relative to non-polar solvent were observed for the excited molecule except the excited states 3 and 7 that are associated with blue (hypsochromic) shifts and high excitation energies. This also confirm that the UV-absorption of the molecule is associated with both π-π* and n- π* transitions as reported in the experimental results (Munish *et al*., 2004; Kalsi, 2005).

Furan-3,4-dicarboxylic acid

The electronic spectra of the compound and its summerized molecular properties (as presented in Figure 4.3 and Tables 4.1) has one band in dichloroethane, dichloromethane, heptane and cyclohexane; two bands were observed in methanol and ethanol while three were observed in tetrahydrofuran. Band IV which appears as shoulder at shorter wavelength region of band III is shifted to shorter wavelength with increasing solvent polarity, an indication that the excited state of this transition has less charged character and less solvated than its ground state. This suggests a specific solvent-solute interaction which may be intra and intermolecular hydrogen bonding interaction between the two adjacent carboxylic (-COOH) groups in the molecules and the polar protic solvent. The appearances of three bands for the spectrum of this compound in tetrahydrofuran show the probability of its strong interaction with this solvent. The intensities of absorption indicated by the calculated molar absorptivities values shown in the Table 4.1 allow band 1 to be assigned $^1A\rightarrow{}^1L_b$, band II as $^1A\rightarrow{}^1L_a$, band 111 as $^1A\rightarrow{}^1B_a$ while band IV is assigned $^1A\rightarrow{}^1B_b$ transition (Platts, 1951; 1953; Iweibo *et al*., 1982; Amrallah *et al*., 2005).

The computed UV-absorption energies (Table 4.15) for the singlet state transitions recorded eight or nine transitions for this compound in the representative solvents (dichloromethane, methanol and n-heptane), signifying lesser overlapping of the transition bands. The excited states with highest oscillator strength occur at the excited state 6 in methanol, and 7 in both dichloromethane and n-heptane. Hypsochromic shift was observed for the compound in methanol. This is an indication of more polar ground state of these transitions and signifies n-π*transitions as specified by the experimental results. This is probably due to specific solvent interaction (i.e both intra and intermolecular hydrogen bonding) of the molecule with methanol (Munish *et al*., 2011) as observed in the experimental results.

3,4- diphenylthiophene

As presented in Figure 4.4 and Table 4.1, the electronic spectra of 3,4-diphenyl thiophene consist of two to five bands depending on the polarity of the solvent. In tetrahydrofuran, acetonitrile, dichloromethane and 1,2-dichloroethane, two prominent bands were observed, three bands were observed in methanol and ethanol while four were observed in heptane, cyclohexane and acetonitrile. These indicate that the bands overlapped to different degrees in different solvent (Kalsi, 2005). The spectra profile of these bands are virtually the same in all solvents used and the bands are designated as $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$ in the order of increasing transition energies. The high values of the molar absorptivities (Table 4.1) of the observed bands except for band I or $S_0 \rightarrow S_1$ in cyclohexane and heptane indicate that these transitions are symmetry or overlap allowed (Silverstein *et al*., 2004). The appearance of two bands in the spectrum of the compound in tetrahydrofuran and three observed bands in methanol, ethanol and acetonitrile is manifested by the overlap of the bands as a result of mixing of their excited states (Munish *et al*., 2011). This is observed for bands $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$. $S_0 \rightarrow S_3$ band where present is not well separated from $S_0 \rightarrow S_4$ band but appears as fused broad shoulder. $S_0 \rightarrow S_3$ band is shifted to shorter wavelength with increasing solvent polarity, while $S_0 \rightarrow S_4$ and $S_0 \rightarrow S_5$ bands shift to a longer wavelength with increasing solvent polarity. This indicates that the excited states of $S_0 \rightarrow S_4$ and $S_0 \rightarrow S_5$ are more solvated than their ground states. These bands may be assigned π -π* transitions (Reichardt, 1988).

Computational results (Table 4.13) recorded ten excited states for the spectra of DPT in the UV-region. Hypsochromic (blue) shifts were observed for all transitions in this molecule with solvent of increasing dielectric constant except for the excited state 2 where the wavelength were retained while red shifts were recorded for the excited state 8 in polar solvent relative to non polar solvent. This signifies that both n-π* and π-π* transitions occur in the compound as indicated by the experimental results. The bands at 43,103 cm^{-1} (in Methanol); 39,370 cm^{-1} (in n-heptane) and 38,991 cm^{-1} (in dichloromethane) recorded in the experimental results are retained in the theoretical results but with slight shift to shorter wavelength due to solvent interactions.

The π-π* transitions which occur as a result of red shift can be ascribed to an increase in contribution of the lone pair of electrons on the electronegative S-atom to the delocalized π-electron system (Varies *et al*., 1997). For this transition, the excited states are more solvated than the corresponding ground state, and the dipole-dipole interaction with the solvent molecules lowers the excited state energy more than the ground state (Reichardt, 1988).

3,4-dicarboxylic-2,5-diphenylthiophene

Three prominent bands were observed in the spectrum of this compound in methanol, ethanol, acetonitrile and tetrahydrofuran, two were observed in 1,2-dichloroethane and dichloromethane, one in cyclohexane while four were observed in n-heptane. These are as shown in figure 4.5 and in the summerized molecular properties of the compound in Table 4.1. This is an indication that the degree of overlap of transition bands of this compound varies from solvent to solvent (Choingwain and Iweibo, 1991). The interaction of ethanol on the compound caused greater distortion of band IV. This is because, in methanol and ethanol, there is probability of the existence of hydrogen bonding between these solvents and DCDPT (Pearson, 1985; Reichardt, 1988; Munisch *et al*., 2011). Moreover, it transition bands lack vibrational fine structure in both polar and non-polar solvents, signifying its greater interaction with these solvents. The disappearance of band I in the spectra of the compound in all solvents except in n-heptane is due to the overlap of band I with band II as a result of the mixing of excited states of bands I and II. The intensities of absorption, as indicated by the calculated molar absorptivities values shown in the Table 4.1 allows band 1 to be assigned $^1A \rightarrow ^1L_b$, band II as $^1A \rightarrow ^1L_a$, band 111 as $^1A \rightarrow ^1B_b$ while band IV is assigned $^1A \rightarrow ^1B_a$ transitions (Platts, 1951; 1953).

The computational data of the UV-studies on this compound recorded bathochromic shift for all the observed transitions except the excited states 2 and 5. This indicates greater charge distribution and increasing delocalization of electrons as a result of extention of conjugation and greater charge transfer phenomena in this compound. The low intensity and red shift of most of the observed excited states (except bands 2 and 5) in polar solvent relative to non-polar solvent indicates the π-π^* nature of these bands (Munish *et al.*, 2004; Kalsi, 2005).

Benzo[b]thiophene

The representative electronic spectra of BT and the summary of the spectral properties of this compound in various solvents are as presented in Figures 4.6 and Table 4.1 respectively. Five distinct bands were observed in methanol and ethanol as solvents, four bands were in heptane, tetrahydrofuran, acetonitrile, dichloromethane and 1,2-dichloroethane while two were observed in cyclohexane as solvents. These bands are designated as $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$, $S_0 \rightarrow S_4$ and $S_0 \rightarrow S_5$ in the order of increasing energies. The intensities follow the order $S_o \rightarrow S_4 > S_o \rightarrow S_5 > S_o \rightarrow S_3 > S_o \rightarrow S_2 > S_o \rightarrow S_1$. From the evidence of single and double excitation configurational interaction (S-CI and D-CI), $S_o \rightarrow S_1$ can be assigned to ^1L_a, $S_o \rightarrow S_2$ can be designated as ^1L_b, $S_o \rightarrow S_3$ corresponds to ^1B_b, while $S_o \rightarrow S_5$ and $S_o \rightarrow S_4$ are assigned the ^1C_b and ^1B_a respectively (Platts, 1951; 1953; Amrallah *et al.*, 2005). The band features of thiophene ($\bar{\upsilon}_{max}$= 42,000 cm^{-1}) and benzene ($\bar{\upsilon}_{max}$ = 39,370cm^{-1} and 49,019 cm^{-1}) are retained in benzo[b]thiophene with slight shift in the absorption band maximum due to increasing conjugation as a results of the condensation of the benzene ring system to position b of the thiophene ring (Finar, 1973). The extra bands represented by ^1C_b in the BT relative to thiophene and benzene moieties is opened to the interpretation expected from the prediction of Free Electron Molecular Orbital (FEMO) theory of Platts, which stated that the enlargement of the pi (π) electron system of benzene ring causes the electronic bands to be remarkably shifted to the red, as a result of which a band occurring in the far ultraviolet region now appears as extra bands in the near ultraviolet (Platts, 1953; Finar, 1973).

Bands I ($S_o \rightarrow S_1$) and II ($S_o \rightarrow S_2$) are not strongly affected by solvent polarity, while bathochromic shifts were observed for bands III and V in solvent of increasing dielectric constant, attesting to their excited states being more solvated (polar) than their ground states. This is an indication of π-π* transitions nature of these bands. Hypsochromic shift was observed for $S_o \rightarrow S_4$ band with increasing solvent polarity, suggesting its n -π* origin. This transition suggests a specific solute-solvent interaction viz, dipole-dipole or hydrogen bonding interaction in the molecule. The appearance of two or four bands in some solvent is probably due to different degree of overlap of the transition bands in different solvent, mixing of excited state of the forbidden transitions with the more allowed transitions or the non transparency of the solvent to the UV light at which some bands occurred (Munish *et al*., 2011). This is indicated by a very weak shoulder appearing at the lower wavelength region of $S_o \rightarrow S_4$ band in the spectral of tetahydrofuran and band $S_o \rightarrow S_5$ which is marred by solvent in the spectra of acetonitrile.

The result of the computational studies on the effect of solvents on the UV spectra band system of this compound as presented in Table 4 .12 shows seven singlet excited states for the compound. This is an indication that the spectra of this compound in the representative solvents are well resolved computationally. The highest peaks are in the wavenumber range of 45,510 cm^{-1} - 49,142 cm^{-1}. The strongest transition observed at 49,142 cm^{-1} in methanol, 48,979 cm^{-1} in dichloromethane and 48,842 cm^{-1} in n-heptane suggest a blue shift (hypsochromic shift) in solvent of high polarity (methanol). This transition is therefore assigned n-π* transition as a result of solvent interaction (intermolecular hydrogen bonding) with the lone pair of electron on the S-moiety on the molecule. This was also observed for other transitions, suggesting that the ground state of the transitions being more polar than their corresponding excited states in polar solvent relative to non-polar solvent (Munish *et al*., 2011). No π-π* transition or red shift recorded in experimental results is observed computationally but the band feature of benzene (49,019 cm^{-1}) and thiophene (42,101 cm^{-1}) reported in experimental results are also recorded computationally but with slight shift to longer and shorter wavelength respectively.

5. 2. Oscillator strength

5. 2. 1. Solvent effect on the oscillator strength

Presented in Table 4.1 are summaries of the transition intensities which are recorded in the form of oscillator strength in different solvents for the various transitions of the compounds studied. The oscillator strength of any electronic transition for compounds in a given solvent $f_{aio(\mathrm{s})}$ increases with increasing solvent polarity (Iweibo *et al*., 1990). This is particularly true for most electronic transitions for the given compounds studied except in 2,3-diphenylcyclopropenone. This trend is in harmony with expectation, as in polar solvent, all the weak interaction forces between the solute and the solvent (the dispersion interaction included) are in operative in the perturbation of the oscillator strength (Praveen and Ojha, 1999). This trend was also observed for the vapour phase oscillator strength $f_{aio(\mathrm{v})}$. The observed deviation in this trend for the oscillator strength for electronic transitions of the 2,3-diphenylcyclopropenone may be owing to complication of number of effects; the intermolecular charge transfer contributions to intensities, mixing of the neighboring excited states and the specific interaction (weak intermolecular hydrogen bonding) between the solute and the solvent (Iweibo *et al*., 1990; Munisch *et al*., 2011).

The vapour phase oscillator strength $f_{aio(\mathrm{v})}$ values for the various bands in all the compounds studied are lesser than those in solution $f_{aio(\mathrm{s})}$ except in few cases where they are equal. This is in agreement with the prediction of equations *2.5* and *3.3*. It shows that these equations have adequately correlated the spectral properties of the molecules in solution with those of the vapour. It is also observed from Table 4.2 and the representative spectra of these compounds in different solvents (Figures 4.1-4.9) that generally for the various electronic transitions in the studied compounds, the magnitude of the oscillator strength (which ranged from $1.40\mathrm{x}10^{-3}$ for the forbidden electronic transition to approximately 1.55 for the fully allowed transition) does not follow the trends described by the theoretical predictions and the molecular orbital calculations of the oscillator strength (Abe and Iweibo 1985a). The experimentally determined oscillator strength for the compounds in solution and those calculated in vapour phase generally follow the trend: $f_{(s_0\rightarrow s_1)} < f_{(s_0\rightarrow s_2)} < f_{(s_0\rightarrow s_4)} < f_{(s_0\rightarrow s_3)}$ or $f(_{(s_0\rightarrow s_1)} < f_{(s_0\rightarrow s_3)} < f_{(s_0\rightarrow s_4)} < f_{(s_0\rightarrow s_2)}$ instead of $f_{(s_0\rightarrow s_1)} < f_{(s_0\rightarrow s_2)} < f_{(s_0\rightarrow s_3)} < f_{(s_0\rightarrow s_4)}$.

The solvent correction factors ϕ to oscillator intensity attributed to the optical set–up in the spectrophotometer and described by the equation *3.3* has varied contributions to the oscillator strength (*f*) of different electronic transitions (Iweibo *et al*., 1990). The fractional contribution of solvent correction factor to the intensity, *q,* as expressed by Abe and Iweibo, (1985a) in the form $q = \frac{\Delta f}{f_s}$ generally follows the trend $q\ (S_0 \rightarrow S_1) > q\ (S_0 \rightarrow S_2) > q\ (S_0 \rightarrow S_4) > q\ (S_0 \rightarrow S_3)$, showing that the more allowed a transition, the less important is the correction factor. For example, benzo[b]thiophene in methanol, $q(S_0 \rightarrow S_1) = 5.0\%$, $q(S_0 \rightarrow S_2) = 3.0\%$, $q(S_0 \rightarrow S_3) = 2.8\%$ and $q(S_0 \rightarrow S_4) = 2.5\%$. The percentage contribution of this correction factor in different compounds varies in different compounds but the same trends were observed.

The small values of the oscillator strength are in conformity with the degree of forbiddance of the transitions and the proximity of the bands to the transition it can borrow intensity from. The S_o–S_1 or ^1L_b transitions are forbidden both quantum mechanically and by parity while the S_o–S_2 or ^1L_a transition is quantum mechanically forbidden but parity or overlap allowed. These bands observed in some of the spectra of these compounds, especially in BT, PQ and DPT are expected for most benzene derivatives, but the deviation of the magnitudes of the oscillator strength for the different transitions from the theoretical descriptions are probably associated with the following reasons (Abe, 1970; Myer and Birges, 1980; Iweibo *et al*., 1990):

a. The vibrational borrowing of intensity from more allowed transitions.
b. The removal of the overlap forbiddance by substitution which mixes the higher adjacent states and sometimes changes the symmetry.
c. The intensity borrowing from solvent transitions.

The oscillator strength greater than unity observed in ^1B_b and ^1B_a transitions of DPCP, DCDPT and PQ in tetrahydrofuran, dichloromethane, cyclohexane and ethanol signify that more than one optical transitions are contributing to the intensities of these bands in these solvents (Iweibo *et al*., 1990). The evidence for the overlap of bands due to mixing of the excited states comes from the observed inflections in the S_o–S_3 and S_o–S_4 bands of these molecules in the named solvents (Lesi, 1996)

The computational results presented in Tables 4.10-4.15 show that for the excited states observed for the absorption spectra of the compounds studied, transition intensities (*f*) are small in conformity with the degree of forbiddance of the transitions. This decrease with decreasing solvent polarity except in few cases where there are exceptions. For all the compounds, PQ recorded the highest oscillator strength associated with all its transitions in all solvent followed by DCDPT. This indicates that greater charge distributions are associated with the excitations of their electrons (Praveen and Ojha, 1999; Karakas, 2010).

5. 3 Substituents effect

5.3.1 Comparison of the effect of substituents on the transition properties ofthiophene derivatives.

In this study, thiophene derivatives (DCDPT; DPT and BT) form the basis of comparison in discussing the effect of substituents on the electronic absorption spectra properties of the molecules. The spectral depicting the effect of different substituents on the absorption frequencies of thiophene derivatives studied is as presented in Figure 4.7. The summary of transition energies ($\upsilon\ cm^{-1}$) and oscillator strength of these compounds are also presented in Tables 4.1 and 4.2. There are four or five bands in the spectra of BT in different solvents (except in cyclohexane) relative to other two thiophene derivatives where maximum of four bands are present (except DPT in n-heptane and cyclohexane). The increase in number of bands in BT is probably due to the enlargement of pi electron system and increasing conjugation in thiophene system by the fused benzene ring on position b of BT moieties (Platts, 1951; Amrallah *et al*., 2005) or the variation in overlap of transition bands in different solvents. These results in bathochromic shifts of λ_{max} relative to DPT and a decrease in the oscillator strength of the various transitions observed for the compound in most solvent relative to other two substituted thiophene compounds. This trend is also observed in the spectra of DCDPT compared with those of DPT. The bathochromic shifts in the peaks wavelength of the DCDPT are due to the extended π-electron manifolds of the two –COOH in conjugation with the substituted thiophene moiety. It can be inferred from this observation that the greater the number of substituents on any system, the greater the oscillator strength (Platt, 1951; Reichardt, 1988). Also, with Platt's Free Electron Molecular Orbital theory, the expansion of the size of π-electron system with a greater number of substituents will not only cause greater ease of shift of an electronic charge (e_i) on a π-electron atom but increases the distance (r) through which such charge is transferred to another atom.

Also, the higher probability of hydrogen bonding between DCDPT and protic solvents (methanol and ethanol) than the other thiophene derivatives studied probably caused the observed transitions of band III and IV for the compound to be of the same wavelength as those of DPT (Pearson, 1985; Munisch *et al*., 2011).

The computational results (Tables 4.12-4.14) show the different excited states of the compounds as a result of the different perturbation effects of substituents on the electronic absorption spectra of these compounds also indicate great changes in their band positions and intensities. Relative to BT, the electronic transitions of DPT increase slightly towards the longer wavelength and higher intensity (bathochromic and hyperchromic effects) in both polar and non polar solvents. This is probably due to the extended conjugation from the phenyl rings. The additional substituents (electron withdrawing) on the DPT ring (as in DCDPT) also have profound influence on its spectral parameters (excitation energy, band position and intensity). Bathochromic shifts were recorded for all the transitions in DCDPT (except the excited states 2 and 5) relative to DPT and BT. This is probably due to greater charge distribution with increasing delocalization of electrons as a result of extention of conjugation and greater charge transfer phenomena in this compound relative to other thiophene derivatives studied (Karakas, 2010). The π-π* nature (as a results of bathochromic shift) of the excited states 2 and 5 is an indication of the stability of the polar excited states of the molecules relative to the ground states as the polarity of the solvent medium increases (Munish *et al*., 2011).). The recorded bands in the wavelength (in wave-number) regions of 43,103 cm^{-1} and 43,103 cm^{-1} (in Methanol); 39,370 cm^{-1} (in n-heptane) and 38,991 cm^{-1} (in dichloromethane) in experimental results are also retained in the theoretical results but with slight shift to shorter wavelength.

5. 4 Transition dipole moments and transition polarizabilities.

As can be seen from Tables 4.3-4.9 for the few solvents where the spectra of the compounds are having more than three bands, the transition polarizabilities (a measure of sensitivity of different transition or system to applied electric field) follow the order oscillator strengths of each transition i.e $\alpha\,(_{(s_0 \rightarrow s_1)} < \alpha\,(_{(s_0 \rightarrow s_2)} < \alpha_{(s_0 \rightarrow s_4)} < \alpha_{(s_0 \rightarrow s_3)}$ or $\alpha_{(s_0 \rightarrow s_1)} < \alpha_{(s_0 \rightarrow s_3)} < \alpha_{(s_0 \rightarrow s_4)} < \alpha_{(s_0 \rightarrow s_2)}$. This trend conforms to the expectations as submitted by Hirschfelder (1954) and Iweibo *et al*., (1990), and supported by the perturbation theory which relates the polarizability α of any state *ij* to the transition frequency (ω_{ij}) between the state *I* and *j* and the oscillator strength f_{ij} by: $\alpha_{ij} = \dfrac{e^2}{m_e} \sum_j \dfrac{f_{ij}}{\omega_{ij}}$ where *e* and m_e denote the electronic charge and mass respectively, and $\omega_{ij} = 2\pi\upsilon_{ij}$ denotes the circular frequency. These trends are reflective of the oscillator strength values for these transitions, and also confirm the positive correlation between the transition polarizabilities ($\Delta\alpha$) and the integral Einstein coefficient K_{jis} (Equation 3.6). In addition, FEMO theory stated that the polarizability is proportional to the molecular volume (i.e. $a^3 = \frac{1}{4\pi\varepsilon_0}\alpha$), where *‘a’* and ε_0 denotes molecular radii and permeability constant respectively (Appendix 3). Consequently, compounds with larger molecular radii show greater transition polarizability (Iweibo *et al*., 1982). The molecular radii follow the trend 2,3-diphenylcyclopropenone < 9,10-phenanthrenequinone, and benzo[b]thiophene < 3,4-diphenylthiophene < 3,4-dicarboxylic-2,5-diphenyl thiophene so do their transition polarizabilities (Rowland and Taylor, 1996). The present analysis agrees favourably with that of Abe and Iweibo (1985) and reconfirms the earlier result of Abe and Amako (Abe *et al*., 1965) but disagrees with` that of Morales (1982). The disagreement with Morales findings probably arises because Morales considered only the dispersion forces in deriving his expression while the present study takes into consideration all possible interaction modes.

The deviation from the order of increasing transition polarizability with oscillator strength for the different transitions in 2,3-diphenylcyclopropenone is probably due to the mixing of the allowed states of this compound with its forbidden states; the latter thus acquiring the characters of the allowed states (Iweibo *et al*., 1990). Moreover, in this strained-ring compound, there is intra-molecular donor-acceptor charge transfer in which there is shift of electron from the phenyl rings through the cyclopropenyl ring to the oxygen atom of the carbonyl carbon (CO).

As observed in Tables 4.3-4.9, the transition polarizabilities (Δα) are positive and small. The small values of the transition polarizabilties of these compounds which represent little or no change in the potential energy surface of the ground and the excited state is in agreement with the conclusion that the equilibrium nuclear position (from the consideration of shape of Franck-Condon envelop) of the excited states is only a little shifted relative to that of the ground state. This shows that there is only a slight reorientation of the solvent molecule which results in a shift between the energies of ground and the excited states. These results are consistent with the reaction field formulation of Liptay (1969; 1974). The observed positive values for the transition polarizabilities (Δα) also show that the excited states of the compounds studied are more polar than their corresponding ground states and that the molecules are chemically active (Iweibo *et al*., 1982; Abdul-Raheem *et al*., 2010; Homocienu, 2011).

The transition dipole moment of the compounds studied (Table 4.4-4.9) follows similar trend observed for the oscillator strength and transition polarizabilties. This order conforms to the expectation as it agrees perfectly with the expression that relates the intensity *I*, of a transition to the square of integral of transition moment, *M*, i.e. $I \,\alpha\, |M_{ij}|^2 = <\mu_i|e_i r_i|\mu_j>^2$ This implies that the more allowed a transition is, the higher the probability that transition dipole moments ($\Delta\mu$) will be greater than zero (Iweibo *et al*., 1982).

Hence, the transition moment integral shows gradation of values, being smallest for the weak and forbidden transitions but increases considerably for the fully allowed transitions. The small but positive values of $\Delta\mu$ (Tables 4.4-4.9) observed for all the transitions in these compounds also point to the conclusion that the equilibrium nuclear position of the excited states of these molecules are a little shifted relative to that of the ground state. However, for band $S_0 \rightarrow S_2$ of the electronic transitions of DCDPT in tetrahydrofuran, band $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_5$ of the electronic transitions of PQ in ethanol, the transition dipole moments ($\Delta\mu$) is greater than one. The high values of this parameter in these solvents are enhanced by increased charge distribution of the π-electrons system in the compounds (Udhayakala *et al*, 2011).

The calculated transition dipole moment values ($\Delta\mu$) for the different transitions from the computational data (Tables 4.16) are functions of the oscillator strength (*f*) values. The higher the *f*, the larger the dipole moment for each compound as confirmed by the experimental results and supported by the perturbation theory (Choingwain and Iweibo 1982). The excited states dipole moment and polarizability are also presented in Tables 4.17-4.20. DCDPT recorded the highest μ^* and α^* (which increase with a decrease in optical gap) among the studied thiophene derivatives. This is attributed to the increase in size of the molecules as substituents on the conjugated system increases. In comparison with experimental estimation, the calculated increase in μ shows the strong activity of these thiophene compounds with DCDPT being the highest (Nadaf, 2004; Islam *et al*., 2011). The presence of ICT character of the singlet state is also reflected by the increase in the dipole moment and lower values of orbital gap of DCF; DPCP and DCDPT (Homocienu *et al*., 2011).

In summary, the result show that the activities of the studied hetero-aromatic molecules on the basis of their sizes, energy gap and polarizability values follow the trend: DCDPT > BT > DPT > DCF. This trend signifies that DCDPT would probably be the most reactive compound of the studied molecules, as well as, exhibiting the highest electro-optical responses on the basis of its largest size, least energy gap and largest polarizability. For the carbonyl derivatives studied, PQ exhibits higher activity due to its larger size, higher dipole moment and polarizability than DPCP (Homocienu *et al*., 2011; Islam *et al*., 2011).

5.5 LUMO - LUMO energy gaps and related molecular properties.

The LUMO - HOMO energy gap reflects the chemical activity of the molecules (Eric *et al*., 2007; Bo *et al*., 2011).The LUMO is an electron acceptor and it is related to the electron affinity of molecule(s) whereas the HOMO represents the ability to donate electron(s) and is related to the ionization potential (Kavitha, 2010). Consequently, a HOMO→LUMO interaction implies the movement of electrons to or from the aromatic parts of the studied molecules, the substituents on the ring system of molecules and the lone pairs of electrons on the S or O atoms of the thiophene or furan moieties. Associated within the frame work of self consistent field molecular orbital (SCF-MO) theory, other molecular properties can be expressed through the E_{HOMO} and E_{LUMO} (optical gaps) as expressed in equations 2.60-2.66. The larger the optical band gaps, the harder the molecules and electron charge transfer is most when the optical band gap is low (Lin *et al*., 2005; Eric *et al*., 2007; Ya-Ying *et al*., 2008). Thus, the calculated values of $\varkappa$, EA, IE, η, χ, ω and S expressed through HOMO and LUMO energy values for the molecules whose optimized structures are in figures 4.15-4.20 are as presented in Tables 4.18-4.20.

For all the molecules, the HOMO, LUMO and the optical band gaps has been found to be closer in methanol and dichloromethane, but differ on changing to n-heptane. This shows that these properties are greatly influenced by solvent polarity (Lin *et al*., 2005). These are found to be higher in polar solvent relative to non-polar solvent, except in PQ and DCF where the transitions are associated with decrease in optical gaps with increasing solvent polarities. This indicates that the electron distribution, conductivity, and the activities of PQ and DCF compounds are enhanced in polar solvents (Lin *et al*., 2005; Ya-Ying *et al*., 2008).

The observed trend in the optical band gaps for the studied thiophene and carbonyl derivatives in the representative solvents are DCDPT < BT < DPT and PQ < DPCP respectively. These further attest to the high conductivities and greater charge distribution associated with DCDPT and PQ molecules as previously reported in section 5.4.   This is because, with the extended conjugation of these compounds and their larger sizes, the

HOMO-LUMO orbitals are closer (Lin *et al*., 2005). This observation agrees favourably with the experimental results in this work.

Also from Tables 4.18-4.20, the electrotronegativity (χ) values of these molecules in the representative solvents follow the trend $\chi_{\text{n-heptane}} < \chi_{\text{DCM}} < \chi_{\text{methanol}}$ (i.e increases with increasing solvent polarity) except in PQ and DCF where it remained unchanged in both polar and non-polar solvents. Similar trends were also observed for IE, η. In all the solvents, χ values are relatively higher in DCDPT compare with other thiophene derivatives, attesting to its stronger affinity for electrons.This is also indicated by its relatively higher electron affinity (EA) and chemical potential (ϗ,) values when compare with other thiophene molecules studied. However, for the three thiophene derivatives, the global handness (η) is lowest in DCDPT in all the solvents. And, associated with these is the relatively higher global softness (*S*). Similar trends were also observed for PQ amongst the carbonyl derivatives.This is an indication of their high chemical activities (Lin *et al*., 2005; Ya-Ying *et al*., 2008). These values indicate that DCDPT is a better candidate for the development of organic photovoltaic cell than the reported DPT (Yohannes *et al*., 2004; Eric *et al*., 2007; Bedeloglu *et al*., 2010).

CHAPTER SIX

SUMMARY AND CONCLUSION

Because of the potential applications of some hetero-aromatic and carbonyl compounds with their derivatives in researches, pharmaceutical and dye industries, their photophysical properties have been systematically investigated in this work. The modified Solvatochromic Shift Equation (SSE) gave results that showed acceptable estimate of the values of transition polarizabilities and transition moments for the studied compounds. Density functional theory with TD-DFT B3LYP/6-31G* levels have been found to provide support for the experimentally observed electronic properties of the systems studied in this work within the experimental errors, solvent interactions and various assumptions and simplifications made in the derivation of the modified solvatochromic shift equation whose consistency has been determined are considered.

The values of oscillator strength in vapour and solution phase have also verified the facts on intensity borrowing from solvents and substituents in the studied molecules. This method gave results that showed more acceptable estimate of the values of transition polarizabilities and transition moments for the studied molecules and the strong activities of the molecules, most expecially, 3,4-dicarboxylic-2,5-diphenylthiophene and 9,10-phenanthrenequinone. New band designated as ^1C_b was found for the spectra of benzo[b]thiophene. The values of the quantum chemical descriptors [optical band gaps ($E_{LUMO-HOMO}$), ϰ, IP, η, χ, ϖ and S] show that polar solvents stabilized the observed transition bands of studied compounds relative to non-polar solvents except 9,10-phenanthrenequinone. 3,4-dicarboxylic-2,5-diphenylthiophene has more photovoltaic application than the reported 3,4-diphenylthiophene as affirmed by the global softness and chemical potential values. Computational results also revealed that the observed electronic transition bands are well resolved and there is minimal overlapping of the transition bands. Moreover, the solvents perturbation allows the assignment of the transitions in these compounds to be both n→π* and π→π* transitions.

In conclusion, Time Dependent Density Functional theory (TD-DFT B3LYP/6-31G* levels) results has been found to provide support for the observed electronic properties of the molecules studied in this work when the experimental errors, solvent interactions and various assumptions and simplifications made in the derivation of the modified solvatochromic shift equations whose consistency has been determined are considered. And, since the transition polarizabilities, transition dipole moments and other quantum chemical descriptors (ϰ, EA, IE, η, χ, ϖ and S) determined for these compounds in this work are being determined for the first time using these methods, it is expected that the results obtained will form a database or use for comparison with the results of future determination by electro-optical and other molecular orbital calculation method.

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AppendixIII: Calculated Onsager radius for the investigated compounds in different solvent

Solvent/compounds	DPCP (10^{-8}) cm	PQ (10^{-8}) cm	DCF (10^{-8}) cm	BT (10^{-8}) cm	DPT (10^{-8}) cm	DCDPT (10^{-8}) cm
Ethanol	4.695	4.710	4.279	4.069	4.914	5.460
Methanol	4.694	4.706	4.274	4.965	4.908	5.456
Acetonitrile	4.702	4.717	4.285	4.075	4.920	5.468
Tetrahydrofuran	4.512	4.526	4.112	3.910	4.721.	5.247
Dichloromethane	3.950	3.962	3.560	3.423	4.133	4.593
Dichloroethane	4.044	4.057	3.686	3.505	4.232	4.703
n-heptane	4.925	4.941	4.488	4.268	5.154	5.727
cyclohexane	4.716	4.731	4.298	4.087	4.935	5.484

Onsager radius (a) was calculated using the equation:

$$a^3 = \frac{3M}{4\pi N_0 d} = \frac{3M_R}{4\pi N_0}\left(\frac{n^2+2}{n^2-1}\right)$$

M is the molecular weight, d density of solvent, M_R molar refraction, n solvent refractive index and N_0 the Avogadro's constant