ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

DEPARTMENT OF CHEMISTRY

Computational study on the Thieno[3,4-b]pyrazines and its derivatives based conducting polymers

By

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June, 2014

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This is to certify that the thesis prepared by Wasihun Menberu, entitled: “**Computational study on the Thieno[3,4-b]pyrazines and its derivatives based conducting polymers**” and submitted in partial fulfillment of the requirements for the degree of Degree of Masters of Science in Chemistry (Physical Chemistry) complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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Examiner	Signature	Date

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This thesis is my original work, has not been presented for a degree in this and other University and that all resources and materials used for this thesis have been duly acknowledged.

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This project has been submitted for examination with my approval as university advisor.

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June, 2014

DEDICATION

I dedicate this thesis manuscript to my family and best friends (G11) for their affection, love and moral support during my study.

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List of Abbreviations

AM1	Austin Model 1
BLA	Bond length alteration
B3LYP	Becke's three parameter exchange Functional with Lee-Yang-Perdew
CNDO	Complete Neglect of Differential Overlap
DFT	Density Functional Theory
Eg	Band gap
GTOs	Gaussian Type orbitals
HF	Hartree-Fock
HOMO	Highest Occupied Molecular Orbital
INDO	Intermediate Neglect of Differential Overlap
ICPs	Intrinsically conducting polymers
LDA	Local Density Approximation
LUMO	Lowest Unoccupied Molecular Orbital
MO	Molecular orbital's
MNDO	Modified Neglect of Differential Overlap
NDDO	Neglect of differential Diatomic Overlap
O.S(f)	Oscillator strengths
PM3	Parametric Model Number 3
Ref	Reference
RHF	restricted Hartree-Fock
SCF	Self – consistent field
STO	Slater Type Orbital
TD-DFT	Time-Dependent Density Functional Theory
TP	Thieno[3,4-b]pyrazines
UHF	unrestricted Hartree-Fock
UV-Vis	Ultra-Violet and Visible
ZDO	Zero differentials overlap

Abstract

The research in the (thieno[3,4-b]pyrazine, TP) π -conjugated molecules has become one of the most interesting topics in the fields of chemistry. The use of low band gap materials is a viable method for better harvesting of the solar spectrum and increasing its efficiency. The control of the band gap of these materials is a research issue of ongoing interest. In this work, the geometrical and electronic properties of (Thieno[3,4-b]pyrazine, [TP]) based donor-acceptor conjugated oligomers were studied by the density functional theory (DFT) at the B3LYP level with 6-31G (d,p) basis set from the geometry optimization the inter-rings bonds are longer than normal double bonds but shorter than the single bonds these indicate that the emerging of a quinoidal like distortions as a result of oxidation. A low band gap will be expected in polymers containing donor-acceptor (D - A) repeating units. The absorption spectra of a designed low-band gap conjugated polymer has been studied using the TDDFT/B3LYP/6-31G. Two main absorption peaks can be seen, the one largest in wavelength corresponding to a HOMO to LUMO transition, except compound ***C1*** *and one involving higher order excitations. The thermodynamic property calculations show that up on polymerization the change in thermodynamic properties decreases. This decrease in change in thermodynamic properties shows that the oxidized forms of the compound* ***(C1)*** *is unstable with compare to other compounds.*

Keyword/phrases: T*hieno[3,4-b]pyrazine(TP), donor-acceptor, low-band gap, optoelectronic, DFT, geometrical and electronic properties*

Chapter 1 Introduction

1.1. Computational Chemistry

The present chapter will be devoted to introducing computational chemistry and its various branches. Computational chemistry can perhaps be loosely defined as chemistry modeling based on a molecular or atomic level description. The term covers a fairly broad range of theories and methods. The various methods of computational chemistry can be thought of as offering a toolbox. For different problems studied choices must be made as to what methods are best suited.

In order to describe microscopic systems, a different mechanics other than the classical mechanics was required. One promising candidate was wave mechanics, since standing waves are also a quantized phenomenon. The fundamental postulate of quantum mechanics is that a so-called wave function, ψ, exists for any system and that appropriate operator which act upon ψ return the observable properties of the system. The operator, that returns the system energy; E, as an Eigen value is called the Hamiltonian operator; $\hat{H}$, thus we write:

$$\hat{H}\ \Psi \ = \ E\ \Psi \qquad (1.1)$$

Which is the Schrödinger equation, can to a good approximation be separated into one part, which describes the electronic wave function for a fixed nuclear geometry, and another part, which describes the nuclear wave function, where the energy from the electronic wave function plays the role of a potential energy. Casting the Hamiltonian into mathematical notation we have:

$$\hat{H} = -\sum_{i}\frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{k}\frac{\hbar^2}{2m_k}\nabla_k^2 - \sum_{i}\sum_{k}\frac{e^2Z_k}{r_{ik}} + \sum_{ij}\frac{e^2}{r_{ij}} + \sum_{i}\frac{e^2Z_KZ_I}{r_{KI}} \qquad (1.2)$$

where I and j run over electrons, k and l run over nuclei, ħ is Planck’s constant divided by 2π, m_e is the mass of the electron, m_k is the mass of nucleus k, ∇^2 is the Laplacian operator, e is the charge on the electron, Z is an atomic number and r is the distance between two particles.

The above Hamiltonian contains pair wise attraction and repulsion terms, implying that no particle is moving independently all of the others. In order to simplify the problem somewhat we may invoke the so-called Born-Oppenheimer approximation. As nuclear are much heavier than electrons their velocities are much smaller. It is therefore assumed that the movements can be decoupled. The energy of the electrons is calculated with the atoms in fixed positions. This approximation is in most cases entirely reasonable and universally applied. The complete Hamiltonian given in Equation 1.2 is then reduced to so called the electronic Hamiltonian, $\hat{H}_e$

$$\hat{H}_e = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j\rangle i}^{M}\frac{1}{r_{ij}} = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} \qquad (1.3)$$

Where $\hat{T}$ and $\hat{V}$ symbols represent for kinetic energy and potential energy, respectively. Indeed a very important consequence of the Born-Oppenheimer approximation is the assumption that the potential energy surface (or the effective force constants) of a molecule is unchanged upon isotopic substitution. The electronic wave function depends parametrically on nuclear coordinates (position of nuclei) but not on their momenta [1]. A physical interpretation can only be associated with the square of the wave function in that $|(\overline{\chi}_1, \overline{\chi}_2, \ldots\ldots\ldots ..\overline{\chi}_N)|^2 d\overline{\chi}_1 d\overline{\chi}_2 \ldots\ldots\ldots\ldots d\overline{\chi}_N$ represents the probability that electrons 1, 2,…, N are found simultaneously in volume elements $d\overline{\chi}_1, d\overline{\chi}_2 \ldots\ldots\ldots\ldots d\overline{\chi}_N$. Hence, the probability of finding N electrons anywhere in space must be exactly unity i.e the wave function satisfying this condition is called normalized. The Born-Oppenheimer Approximation and the variational principle assumptions are important in solving the time-independent Schrödinger equation. The variational principle [2] states that the energy expectation value, E_{trial} of the Hamiltonian operator , $\hat{H}$, from any guessed ψ_{trial} is always greater than (the upper bound) or equal to the true ground-state energy, E_0, of the system.

$$E_{trial} = \frac{\langle \psi_{trial} \left| \hat{H} \right| \psi_{trial} \rangle}{\langle \psi_{trial} \psi_{trial} \rangle} \geq E_0 \qquad (1.4)$$

The equality occurs only when the trial wave function is the true ground-state wave function of the system.

There are many approaches of computational chemistry that are popular in molecular modeling. We can divide these approaches to two broad part, empirical and quantum approaches [3]. Empirical approaches use simple models of harmonic potential, electrostatic interaction, and dispersion forces for basic comparisons of energetic and geometry optimization. Quantum approaches roughly divided into semi empirical methods and non-empirical (or *ab initio*) methods. Semi empirical methods are the approximate methods in which some quantities are taken from experiment, some small quantities are neglected, and some quantities are estimated by fitting to experimental data. *Ab initio* methods do not require empirical parameters and can be used for a lot of molecular systems. *Ab initio* methods use the Hartree- Fock method as a starting point, i.e. the wave function is used to describe electronic structure. Lately, density functional approaches have come into major use at the non-empirical methods [3]. Then the next part summarizes the details of each computational method.

1.2. The *ab initio* (Hartree - Fock) Method

Ab initio (Latin from the scratch) methods use equations that are being derived directly from theoretical principles, with no inclusion of experimental data. The most intermediate contrast with semi-empirical methods is the fact that all integrals are evaluated from the scratch [4]. The most common type of *ab initio* calculation is called a Hartee - Fock calculation, in which the primary approximation is the central field approximation. This means that the coulombic electron-electron repulsion is taken into account by integrating the repulsion term. This gives the average effect of the repulsion, but not the explicit repulsion interaction. This is a variation calculation, meaning that the approximate energies calculated are all equal to or greater than the exact energy. In order to describe the quantum mechanical behavior of all electrons in systems, it is strictly necessary to calculate the many-electron wave functions for the system using the time-independent Schrödinger equation [5, 6]:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}\psi(r) + V\psi(r) = E\psi(r) \qquad (1.5)$$

When the only terms in the Hamiltonian are the one electron kinetic energy and nuclear attraction terms, the operator is separable and may be expressed as

$$\hat{H} = \sum_{i}^{N} h_i \tag{1.6}$$

Where N is the total number of electrons and h_i is the one electron Hamiltonian defined by:

$$h_i = -\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{M} \frac{Z_k}{r_{ik}} \tag{1.7}$$

Where M is the total of nuclei, Z is an atomic number, and r is the distance between two particles ∇^2 is the Laplacian operator. Eigen functions of the one electron Hamiltonian defined above must satisfy the corresponding one electron Schrödinger equation.

$$h_i\psi_i = \varepsilon_i\psi_i \tag{1.8}$$

Because the Hamiltonian operator defined by Equation (1.1) is separable, its many electrons Eigen functions can be constructed as products of one electron Eigen function. That is

$$\psi_{HP} = \varphi_1^*\varphi_2^*\varphi_3^* \ldots\ldots\ldots \varphi_N^* \tag{1.9}$$

The wave function of Hartree - Fock approach is complicated than the Hartree product wave function, but it can be written in a compact way as a Slater determinant. Since electrons are fermions having a spin of ½, the total electronic wave function must be anti symmetric with respect to the interchange of any two-electron coordinates.

The simplest anti symmetric function that is a combination of molecular orbitals is a determinant.The determinant considers the spin of all the electrons and the Pauli Exclusion Principle. The electron scan have a spin up (+1/2 or α) or spin down (-1/2 or β).

The following is an example of a Slater determinant for a system of N-electrons [1, 5 - 7].

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \psi_2(1)\beta(1)\ldots & \psi_N(1)\alpha(1) & \psi_N(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \psi_2(2)\alpha(2) & \psi_2(2)\beta(2)\ldots & \psi_N(2)\alpha(2) & \psi_N(2)\beta(2) \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_1(N)\alpha(N) & \psi_1(N)\beta(N) & \psi_2(N)\alpha(N) & \psi_2(N)\beta(N)\ldots & \psi_N(2)\alpha(2) & \psi_N(N)\beta(N) \end{vmatrix} \qquad (2.0)$$

Where: ψ is the electronic wave function, α and β spin of electrons and $\frac{1}{\sqrt{N!}}$ is a normalization factor.

In the Hartree - Fock (HF) method this is avoided by calculating the energy of each electron in the averaged static field of the others. Initially a guess is made of the electron energies. The energy of each electron is then calculated in the field of the initial electron configuration. This procedure is repeated in an iterative loop until convergence (Self-Consistent referring to this iterative calculation). In that, the orbitals are improved from cycle to cycle until the electronic energy reaches a constant minimum value and the orbital's no longer change with the mean field of other electrons in the molecule. In SCF theory, closed-shell systems are calculated using restricted Hartree - Fock, RHF theory while open shell molecules (with unpaired electrons) use unrestricted Hartree - Fock, UHF formalism. [8]

The Hartree - Fock method can therefore be thought of as a kind of mean-spherical approximation at the electron level. The difference between the Hartree - Fock energy and the energy for the full Schrödinger equation is called the correlation energy. Hartree - Fock calculations are sufficiently accurate to provide insight into many problems and they are widely used. As Hartree - Fock calculations have been applied to different problems it has however become increasingly clear that the correlation energy is of great significance in determining the properties of a system. Efforts have therefore been made to improve on the Hartee - Fock energy.

1.3. Semi-empirical Methods

Semi-empirical methods represent a “middle road” between the mostly qualitative results available from molecular mechanics and the computationally time-consuming quantitative results available from *Ab initio* methods. Semi-empirical methods are a good choice for many users, especially those new to molecular modeling that are less interested in research-quality numerical results, and are more interested in developing their ability to use computing to understand structure, properties, and activities.

The central assumption of semi empirical methods is the zero differentials overlap (ZDO) approximation which neglects all products of basic functions depending on the same electron coordinates when located on different atoms. The earlier semi-empirical MO methods, CNDO, INDO, and NDDO, were developed by Pople et al. at a time when the available computers were able to handle *ab initio* calculations only on the smallest systems. The complete neglect of differential overlap (CNDO) method is the simplest of the neglect of differential overlap (NDO) methods. This method models valance orbital’s only using a minimal basis set of Slater type orbitals. Practically all CNDO calculations are actually performed using the CNDO/2 method, which is an improved parameterization over the original CNDO/1 method. There is a CNDO/S method that is parameterized to reproduce electronic spectra. The CNDO/S method is improved prediction of excitation energies, but at the expense of the poorer prediction of molecular geometry the modified neglect of diatomic overlap (MNDO) method is another semi-empirical method that has been found to give reasonable qualitative results for many organic systems. The MNDO, AM1, and PM3 methods are parameterization of the NDDO model, where the parameterization is in terms of atomic variables, i.e. referring only to the nature of a single atom. MNDO, AM1 and PM3 are derived from the same basic approximations (NDDO), and differ only in the way the core – core repulsion is treated, and how the parameter increases as the square of the number of elements.

1.4. Density Functional Theory (DFT)

Density Functional Theory (DFT) method is the most popular and *versatile* quantum mechanical method available in computational science to investigate the electronic structure of many-electron systems and the total energy is expressed in terms of the total electronic density rather than the wave function. The electron density unlike the wave function is a physically observable quantity. It has been proven that given the electron density the Hamiltonian operator is also determined.

A variational principle has also been established for DFT. Unlike HF theory DFT in itself contains no approximations. There is however no way to derive an energy contribution in DFT known as the exchange-correlation energy. The quality of the models is usually determined by some form of comparison with experimental data. DFT models are therefore in a sense semi - empirical models and once assumptions about the exchange-correlation energy are introduced (as they must be) there is no variational principle. This means that for DFT, unlike HF and post-HF methods, there is no a priori way to establish how good a given method is and no systematic way to improve upon it. In DFT the main focus is not on the N-electron wave function $\Psi(\overline{\chi_1}, \overline{\chi_2}, \ldots \ldots \overline{\chi_N})$ and the associated Schrödinger equation, but instead on the much simpler electron density $\rho(\bar{r})$. The electron density is the number of electrons per unit volume for a given state. It is dependent only on 3 coordinates independently of the number of electrons of the system.

Thus we have that:

$$N = \int \rho(\bar{r}) \overline{dr} \qquad (2.1)$$

DFT is today one of the most important tools for calculating of ground state properties of metals, semiconductors, and insulators. The principal aim of any many-body theory is to reduce the number of parameters needed to describe the system. The exact ground state of the system corresponds to the electronic density for minimal total energy. The total energy functional can be written as [5]:

$$E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] \qquad (2.2)$$

$$= \int \rho(\bar{r}) v(\bar{r}) \overline{dr} + F[\rho]$$

Where:

$$F[\rho] = T[\rho] + V_{ee}[\rho] \qquad V(\bar{r}) = \sum_{A} \frac{Z_A}{|R_A - \bar{r}|}$$

$$V_{ee}[\rho] = J[\rho] + \text{non - classical term} \qquad J[\rho] = \frac{1}{2} \iint \frac{\rho(\bar{r})\rho(\bar{r}')}{|\bar{r} - \bar{r}'|} d\bar{r} d\bar{r}'$$

Here $T[\rho]$ is the total kinetic energy, $V_{ne}[\rho]$ represents the electron - nuclei attraction, and $V_{ee}[\rho]$ represents the electron-electron interaction. $V(\bar{r})$ Is the external potential felt by an electron due to the nuclei. The term $J[\rho]$is the classical columbic electron repulsion term.

Several promising methods of dealing with the problem of strong correlations have been developed in recent years. Kohn and Sham made one of the important advances in the calculation of the energy of density of atoms and the forces on each atom in 1965. They showed how a self - field consistent theory could be applied to this problem. In their method, electron density plays an important role so that, although the term has more general applicability, the Kohn-Sham method is commonly referred to as density functional theory (DFT). The general Kohn-Sham equation is given by:

$$H\psi_i(r) = -\frac{1}{2}\nabla^2\psi_i(r) + V_{eff}(r)\psi_i(r) = \varepsilon\psi_i(r) \qquad (2.3)$$

Where $V_{eff}(r) = V_{ext}(r) + V_{HF}(r) + V_{xc}(r)$ for external, Hartree-Fock, and exchange correlation potentials.

Density functional methods such as local, gradient corrected and hybrid forms have been developed for describing this exchange-correlation.

The Local Density Approximation (LDA) is the basic assumption for almost all approximations currently used in DFT. It is assumed that the density locally can be treated as a uniform electron gas, or equivalently that the density is a slowly varying function. One of the most common DFT methods is the so-called B3LYP method, which is a form of hybrid between DFT and HF methods. It is considered to be fairly robust, perhaps because it balances some of the weaknesses of DFT and HF methods. B3LYP is the DFT method that will be used in this work.

1.5. Basis set in Computational Chemistry

A basis set in chemistry is a set of functions used to create the molecular orbitals, which are expanded as a linear combination of such functions with the weights or coefficients to be determined. Usually these atoms are atomic orbitals, in that they are centered in the two atoms. Atom centered basis sets are comprised of atomic functions representing the electron population at a given distance from the nucleus and can be thought of as being atomic orbitals. There are number of different types of atom centered basis functions available, Slater Type Orbitals (STO) which are the form:

$$R(r) = Nr^{n} e^{\xi r} \qquad (2.4)$$

Where n is the principal quantum number, N is normalization constant, r is the distance from the nucleus and ζ (zeta) is a constant related to the atomic charge of the nucleus. Unfortunately, STOs are often impractical for quantum chemical calculations as some of the integrals are difficult or even impossible. By far the most popular type of basis sets used in quantum chemistry are those based on Gaussian functions, Gaussian Type orbitals (GTOs), these have the form:

$$R(r) = x^{a} y^{b} z^{c} e^{-\alpha r 2} \qquad (2.5)$$

A determines the spread of the function, 'r' is the distance from the nucleus, x, y, z are Cartesian variables and a, b, c determine the order of the function and α is the orbital exponent. The advantage of the Gaussian function is that less computer time is required to evaluate the integrals [5, 8].

For computational reasons Gaussian type orbitals (e^{-r^2}) are commonly used. Gaussian type orbitals do however not has the correct shape required to reproduce the form of an electron distribution. Orbital's are therefore usually constructed as combinations of a set of Gaussians in order to reproduce the correct shape. Basis-sets must be sufficiently flexible to allow the description of electron distribution in various forms of molecules and the quality of the results obtained do in general improve with increasing size and flexibility of the functions employed.

On the other hand calculations will also become more time consuming with increasing basis set size. One of the common approaches is to add more basis sets for the valence electrons compared to inner orbitals. In the present work the common 3-21G* and 6-31G (d,p) basis sets will be utilized. 3-21G indicates a single basis set consisting of 3 Gaussian functions for inner electrons and two separate basis functions, one consisting of 2 Gaussians functions and the other 1 Gaussian function for valence electrons. In 6-31G the number of Gaussian functions to represent the basis sets is increased and. it is common to add further sets of basis functions. One approach is to add higher level orbitals to electrons at a given level; one may for example add d-orbitals to electons in a p-orbital and p-orbitals to electrons occupying s-orbitals. Such orbitals are called polarizable orbitals and the inclusion of such d-orbitals will in the present work be indicated with a (d) and p-orbitals with (p). It is common to indicate the use of polarizable orbitals with a (x, y) notation, where x is the number of polarizable orbitals on heavy (non-hydrogen) atoms and y indicates the polarizable functions on the hydrogen atoms. Another notation that is sometimes used is to indicate (d) polarization with a "*" and (d, p) polarization with "**". This notation is utilized in this work. Finally there is in some cases a special need to allow electrons to localize far from the atom center. Standard basis-sets are in such cases augmented with so called diffuse basis sets. Diffuse basis-sets on heavy (non hydrogen) atoms are indicated with a "+", if they are also included on hydrogen atoms it is indicated with "++". One of the circumstances in which such diffuse basis sets are required is in the accurate modeling of hydrogen bonds. Some basis-sets are regarded as being better than others in providing quality results for a given amount of computational time.

1.6. Ultraviolet (UV) Absorption Spectroscopy

Most organic molecules and functional groups are transparent in the portions of the electromagnetic spectrum called UV/Visible region which ranges from 200 nm to 800 nm. Electronic excited states are most relevant when considering absorption spectroscopy. Molecules can absorb a photon in the UV-Vis range and convert to an electronically excited state. The commonly used law in UV absorption spectroscopy is the Beer-Lambert law which is given by

$$A = -\log T = \varepsilon c l \qquad (2.6)$$

Where the transmittance, T, is the ratio of the intensity of the transmitted to the incident monochromatic radiation, C is concentration (M) and l optical path length (cm) of the sample, ε is molar extinction coefficient ($\mathrm{Lmol^{-1}cm^{-1}}$). An alternative measure of absorption intensity, which can be related readily to theoretical principles, is the Oscillator Strength (the measure of intensity), f, given by:

$$f = 4.315 \times 10^{-9} \int \varepsilon dv \qquad (2.7)$$

The oscillator strength is useful for comparing different transitions. Oscillator strength can range from 0 to 1, or a small integer. A strong transition will have an f value close to 1. Oscillator strengths greater than 1 result from the degeneracy of real electronic systems. The major difference between the oscillator strength (dimensionless), f and extinction coefficient, ε is that f is a measure of the integrated intensity of absorption over a whole band, whereas ε, is a measure of the intensity of absorption for a single wave length. Quantum mechanically this transition moment is related to the oscillator strength as:

$$f = \frac{8 \Pi^2 v_{if} m_e \langle \psi_i | \hat{\mu} | \psi_f \rangle^2}{3 he^2} \qquad (2.8)$$

With m_e is electronic mass, h is Plank's constant and v_{if} is the frequency corresponding to the transition.

1.7. Conducting Polymers

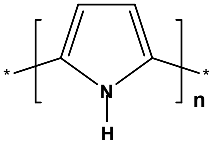
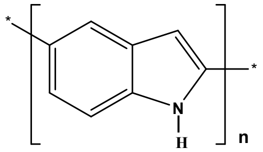
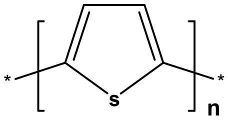
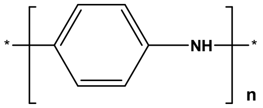
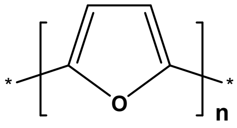
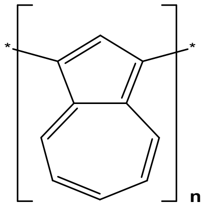
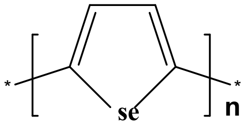
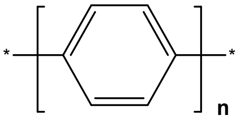
Polymers are macromolecules built up by the linking of large number of much smaller molecules. The smaller molecules that combine with each other to form polymer molecule are termed monomers, and the reactions by which they combine are termed polymerization [9].

Intrinsically conducting polymers (ICPs) are an exciting new class of electronic materials, which have attracted rapidly increasing interest since their discovery in 1979 [10]. ICPs have the potential of combining the high conductivities of pure metals with the processibility, corrosion resistance, and low density of polymers [11]. Additionally, they have many applications in the fields of rechargeable batteries [12, 13], electrochromic display devices [14, 15], electromagnetic shielding [16], sensor technology [17], non-linear optics [18], and molecular electronics [19, 20].

1.7.1. Polyheterocycles as Conducting Polymers

Large-scale interest in conducting polymers is a relatively recent occurrence, although materials that might be considered electrically conductive polymers, such as filled polymers and aniline blacks, were known at the beginning of this century. The current interest in conductive polymers began in the 1970's, when it was found that the electrical conductivity of polyacetylene, a semi-conductor when pristine, could be increased by over fifteen orders of magnitude by treatment with oxidizing agents such as iodine. The synthesis of polyacetylene in the highly conducting doped form was a starting point for a considerable number of studies. Electrodeposition of free standing films of polypyrrole from organic media [21] opened the way to intensive research into polyheterocyclic and polyaromatic conducting polymers [22].

The electrochemical oxidation of these resonance-stabilized aromatic molecules has become one of the principal methods for preparing the conjugated, electronically conducting polymers. Since the first reports of the oxidation of pyrrole, many other aromatic systems have been found to undergo electropolymerization to produce conducting polymers, like thiophene, furan, selenophene, aniline, azulene, indole paraphenylene [23 - 27], as well as many substituted, multi-ring and polynuclear aromatic hydrocarbon systems (Scheme 1). It was found that all of the resulting polymers have a conjugated backbone, which is required for conductivity. Furthermore, these polymers are electrochemically oxidized to their doped states as they are formed. This oxidation necessitates the incorporation of charge compensating anions, also known as dopants, into the oxidized film to maintain electroneutrality.

Polymers	Structure	Polymers	Structure
Polypyrrole		Polyindole	
Polythiophene		Polyaniline	
Polyfuran		Polyazulene	
Polyselenophene		Polypara - phenylene	

Scheme 1: Names and idealized structures of the most widely studied conducting polymers.

Polythiophene is among the widely studied conjugated organic polymers, experimentally and theoretically [28]. Due to its chemical stability, high conductivity upon doping, and their non-linear optical properties, unique electrical properties, ability to exhibit environmental stabilities, the ease of derivatization and ability to be polymerized by a variety of chemical and electrochemical methods [29 - 31]. During the recent years systematic efforts were aimed at investigating the molecular and electronic structure of thiophene oligomers and its derivatives [32, 33].

1.7.2. Synthesis of Conducting Polymers

Conducting polymers can be synthesized *via* chemical or electrochemical routes, although the former has now been largely superseded by electrochemical methods. However, many polymers, most notably polyacetylene, are still only accessible *via* chemical synthesis. The following sections describe these two different synthetic routes.

1.7.2.1. Chemical Synthesis

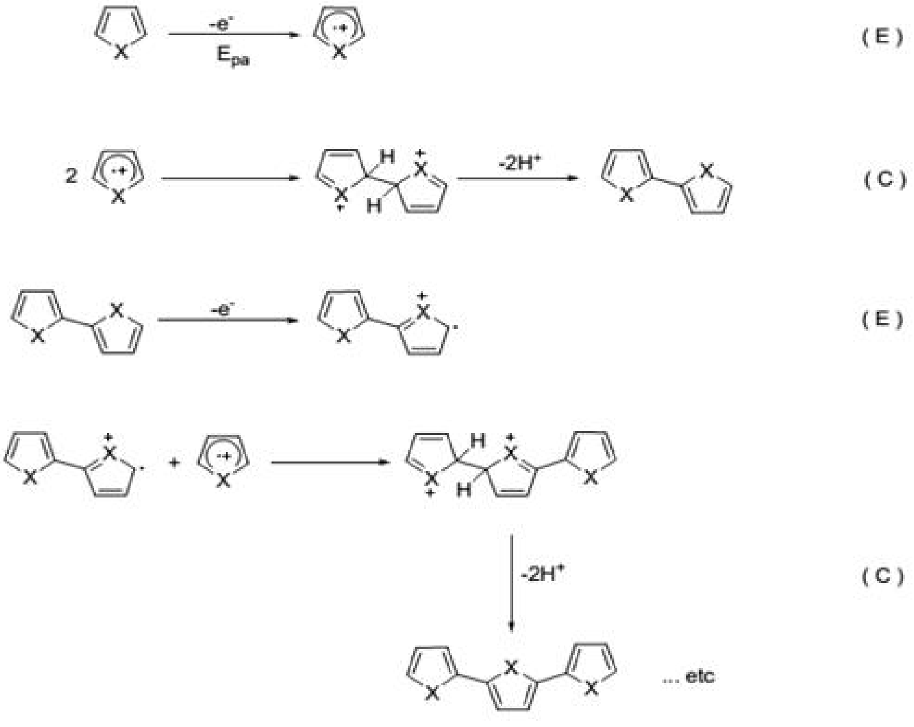
A large number of conducting polymers can be synthesized *via* catalytic oxidation [34, 35]. However, control over polymer morphology is extremely limited, purification can be problematic and processing is virtually impossible.

1.7.2.2. Electrochemical Synthesis

Electrochemical synthesis of conducting polymers offers many advantages over chemical synthesis, including the *insitu* deposition of the polymer at the electrode surface and eliminating processibility problems and the control of the thickness, morphology and degree of polymer doping by quantity of passed charge. In addition, the polymers are simultaneously oxidized to their doped conducting forms during polymer growth. Electropolymerization is achieved by the electrooxidation of the heterocyclic in an inert organic solvent containing supporting electrolyte [36]. A schematic of the generally accepted mechanism for electropolymerization of five membered heterocycles [37] is shown in Scheme 2.

The initial electrochemical step (E) is a one-electron oxidation of the monomer to form its radical cation. A high concentration of these species is maintained at the anode surface because the rate of electron transfer greatly exceeds the monomer diffusion rate to the electrode surface. The second step, a chemical reaction (C), involves the spin pairing of two radical cations to form a dihydro dimmer dication, which subsequently undergoes the loss of two protons and re aromatization to form the dimers. Aromatization is the driving force of the chemical step (C). Coupling occurs primarily through the α– carbon atoms of the heterocyclic ring since these positions have the highest unpaired electron π-spin density and hence reactivity.

At the applied potential, the dimmer, which is more easily oxidized than the monomer, exists in a radical cation form and undergoes further coupling reactions with other radical cations. This electropolymerization mechanism, according to the general scheme E $(CE)_n$, continues until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the anode surface [31]. However, this mechanism of electropolymerization is greatly simplified with regard to the nature of the rate limiting step and the exact role of oligomers in the initial deposition step, which are remaining unresolved [38].



X=S,N,O.......

Scheme 2: Proposed mechanism of the electrochemical polymerization of five membered π-Conjugated Systems.

1.7.3. π-conjugated system

The emergence of conjugated polymers [29] as a new class of electronic materials has attracted considerable attention, since the study of these systems has generated entirely new scientific concepts as well as potential for new technology. Conjugation can occur in any molecule with three or more adjacent atoms with overlapping p-orbitals [39]. Lewis representations of conjugated systems possess alternating single (indicating sigma bonding only) and multiple bonds (where π-bonding is present).

In heavier atoms, d-orbitals can also potentially be involved in conjugation. Delocalization of electrons occurs when π-electrons mobilize across all the appropriately aligned p-orbitals from adjacent atoms. The π-electrons are associated with a group of atoms rather than being localized in either a molecular orbital shared between only two atoms or in an atomic orbital (associated with a single atom).

This phenomenon increases stability by it lowering the ground state energy of the molecule [40]. Due to their unusual optoelectronic properties, a variety of π-conjugated materials have found applications in multidisciplinary fields such as medicinal chemistry, [41], material Science [42], and crop protection science [41]. The optical and electronic properties (such as electrical conductivity and nonlinear optics) of π-conjugated materials are influenced by the strength of conjugation [40, 43]. π - Conjugated polymers and monomers can be employed as photovoltaic cells, [43], light emitting diodes [42, 43] and polymeric sensors [44].

1.7.4. Band Gap Engineering of π-Conjugated Polymers

The discrete molecular orbitals in any extended conjugated system can be divided into stabilized bonding orbitals and destabilized anti - bonding orbitals, resulting in two continuous bands (energy levels) called valence and conduction bands. The valence band is occupied with electrons while the conduction band remains empty.

The energy difference between valence and conduction bands in conducting materials (including conductive polymers) is analogous to the HOMO (Highest Occupied Molecular Orbital)-LUMO (Lowest Unoccupied Molecular Orbitals) gap of small molecules, generally referred to as the energy gap (Eg) [45].

The HOMO-LUMO gap is a very important parameter in defining the optical and electronic properties of materials. When a molecule absorbs energy; the electron gets promoted from an occupied molecular orbital to a vacant molecular orbital at a higher energy. The most probable electronic transition is from HOMO to LUMO, however other transitions can occur, including

$\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and additional $\pi \rightarrow \pi^*$ transitions.

The energy difference between the HOMO and LUMO decreases as conjugation is extended due to relative energies of the increasing number of conjugated π-orbitals (Figure 1). Experimentally, the energy gap can be determined using a UV-VIS spectrometer by identifying the lowest energy absorption edge (λ_{onset}) in the spectrum of the material [45].

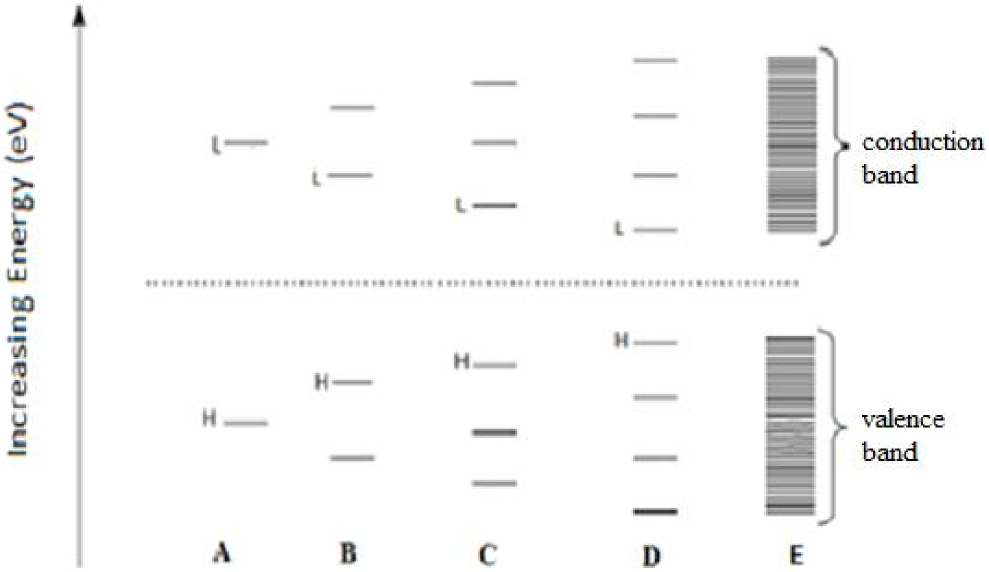


Figure 1: The schematic diagram of LUMO (L) and HOMO (H) demonstrating the effect of increasing π-conjugation from A (2πe-), B (4πe-), C (6πe-), D (8πe-) and E (2nπe-) system [45].

The conjugated molecular orbitals of linear polyenes, such as polyacetylene are delocalized throughout the structure and theoretically, the HOMO-LUMO gap of this molecule could approach zero. However, studies on the effective conjugation length show that there is an upper limit (saturation of monomer units at which conjugation occurs) for the addition of double bonds to linear polymers where no additional effect is observed [45].

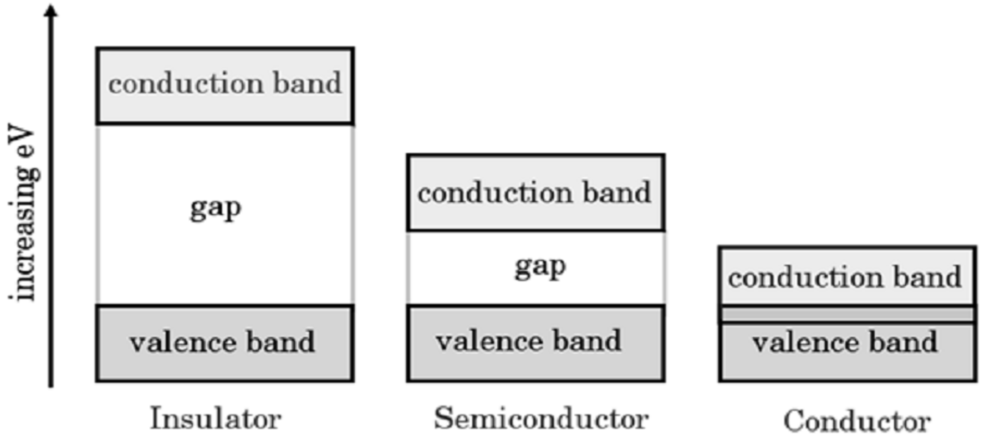


Figure 2: The energy gap comparison of an insulator, semiconductor and conductor [45].

The conductivity of a π-conjugated system is directly dependent on the energy gap; the smaller the energy gap, the greater the conductivity (Figure 2) [45]. Insulators, such as diamond have an energy gap of 5.5 eV, while a semiconductor material such as silicon has 1.1 eV [46]. While the energy gap of any metal will be ≈ 0 eV due to the overlap of the conduction and the valence bands. Conjugation needs to extend over the length of the entire molecule in order to obtain the narrowest possible energy gap. Many studies have been carried out to identify suitable conjugated systems (possessing a small energy gap) that could act as alternatives to metals [45, 47]. Such as polythiophene (Figure 3). The energy gap (Eg) of these linear π-conjugated systems can be influenced by the sum of five structural contributors:

$Eg = E_{BLA} + E_{Res} + E_{sub} + E_{\theta} + E_{Int}$ where BLA represents the bond length alteration; Res, resonance; Sub, the effect of substituent; θ, for dihedral angle; and Int, intermolecular interactions.[47]

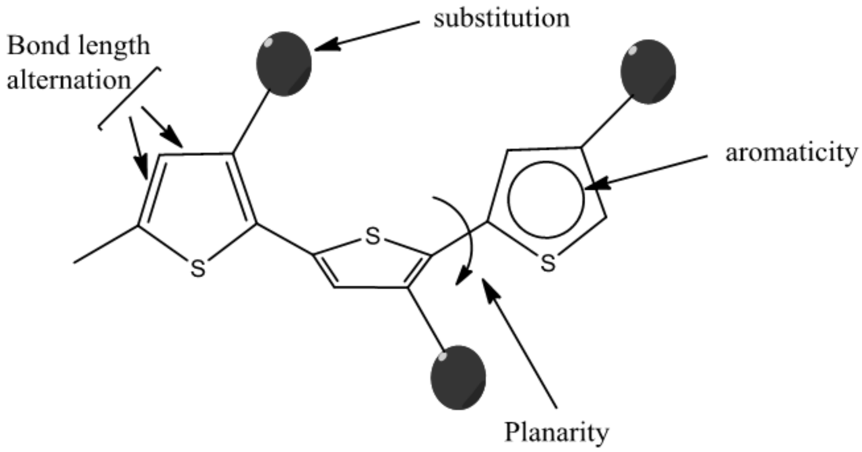


Figure 3: Structural factors that affect the HOMO - LUMO gap of linear π-conjugated systems [47].

E_{Res} confines the delocalization of π-electrons within the aromatic ring while the E_{θ} between the consecutive units limit the π-electrons along the conjugated backbone. The E_{sub} directly modulates the energy levels based on the electron withdrawing or donating substituents. When individual molecules or polymer chains are assembled into a material, the E_{Int} can affect the magnitude of the molecules of the energy gap because each polymer chain experiences weak intermolecular interaction. Therefore, the five energy gap influencers of E_{BLA}, E_{Res}, E_{Sub}, E_{θ}, and E_{Int} are essential parameters to synthetic approaches for conjugated polymer synthesis [47].

1.7.5. Donor–Acceptor π-Conjugated Polymers

A strategy to induce minimum twisted arrangements between consecutive repeating units in conjugated polymers involves construction of A–B type systems where the “A” unit has strong electron-donating and the ‘‘B” unit has strong electron-withdrawing moieties. Interaction of the donor–acceptor moieties enhances the double bond character between the repeating units, which stabilizes the low band gap quinonoid-like forms within the polymer backbones. Hence, a conjugated polymer with an alternating sequence of the appropriate donor and acceptor units in the main chain can induce a reduction in its band gap energy.

Recent molecular orbital calculations have shown that the hybridization of the energy levels of the donor and the acceptor moieties result in D –A systems with unusually low HOMO – LUMO separation [48].

If the HOMO levels of the donor and the LUMO levels of the acceptor moiety are close in energy the resulting band structure will show a low energy gap as depicted in Figure 4. Further hybridization upon chain extension reduces the band gap. During the progress of polymerization, the HOMO and LUMO levels of the repeating unit disperse into the valance and conduction bands.

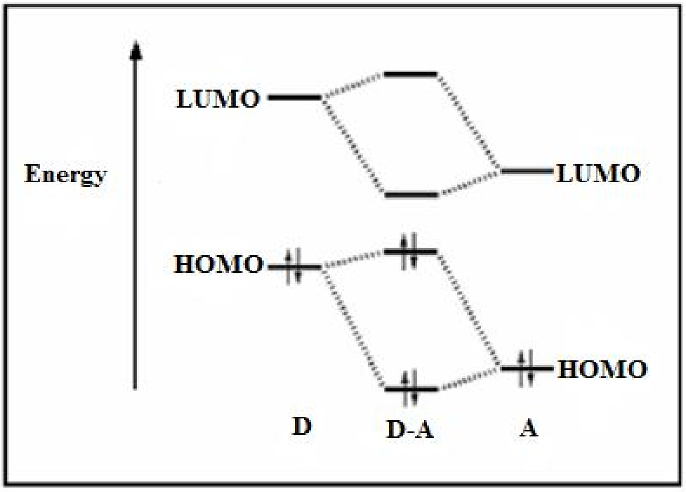


Figure 4: Molecular orbital interaction in donor (D) and acceptor (A) moieties leading to a D –A monomer with an unusually low HOMO –LUMO energy separation [48].

Further reduction in band gap is possible by enhancing the strength of donor and acceptor moieties *via* strong orbital interactions. In donor – acceptor systems, the introduction of electron withdrawing groups reduces Eg by lowering the LUMO levels whereas, the introduction of electron donating groups reduces Eg by raising the HOMO levels. Therefore, designing of extremely low Eg polymers requires strong donors and acceptors. The synthetic principles for lowering the band gap of linear π-conjugated polymers have been reviewed by Roncali [47].

Chapter 2 Objectives

This thesis was performed mainly for the purpose of the following general and specific objectives.

2.1. General objective

The general objective of this study is to make a theoretical investigation on thieno[3,4-b]pyrazines and its derivatives.

2.2. Specific objectives

The specific objectives of this study include:

- ✓ To optimize the geometries and calculate electronic structure of thieno[3,4-b]pyrazines and its derivatives.
- ✓ To compute the UV-Vis electronic transition state of thieno[3,4-b]pyrazines and its derivatives.
- ✓ To compute the thermodynamic properties of the studied compounds.
- ✓ To compare the results of this study with that of literature reports.
- ✓ To identify stable polymers which can be better in conducting polymer materials.

Chapter 3 Computational methods

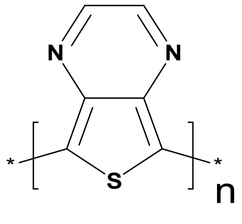
All calculations were done by using Gaussian09W [50]. The compounds of interest were first optimized before any type of chemical properties has been determined.

The geometries of the thieno[3,4-b]pyrazines and its derivatives were optimized at by Becke's three parameter hybrid functional for exchange combined with the correlation functional due to Lee, Yang, and Parr (B3LYP) [1, 50 , 51] level using 3-21G* basis set and further reoptimize using 6-31G(d) basis set . DFT/B3LYP/6-31G (d) has been found to be an accurate formalism for calculating the geometrical, electronic structures and optical properties of many organic molecules [52 - 54]. All the optimizations were done without constraint on dihedral angles. The HOMO, LUMO and band gap (HOMO - LUMO) energies were also deduced for the stable structures.

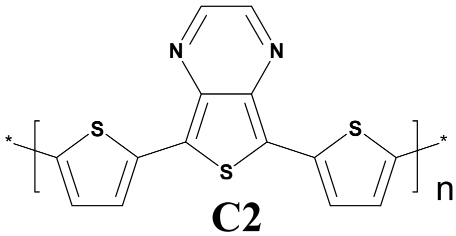
In the UV – Vis electronic transitions, calculations of excited states were performed using the Time - Dependent Density Functional Theory (TDDFT) with B3LYP/6-31G (d) in CCl_4 solvent formalism as implemented in the Gaussian09 code. All the calculations were performed at 298.15 K and 1.00 atm. This project was done using the Intel [R] core(TM) 2 duo CPU Version 2002 computer.

3.1 Compounds Investigated

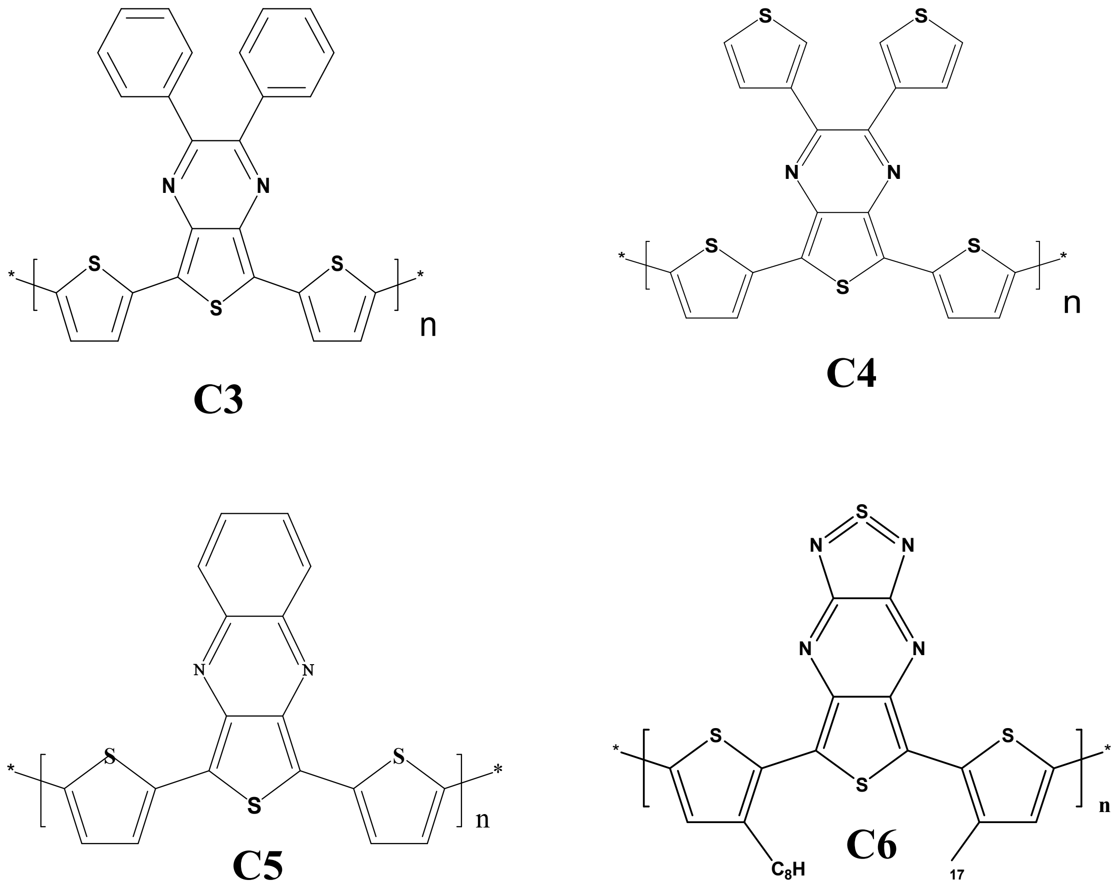
Thieno[3,4-b]pyrazine, [TP] a promising material for optoelectronic devices. Thieno[3,4-b]pyrazines have been shown to be excellent precursors for the production of low band gap conjugated polymers [55-58]. Recently, photovoltaic devices consisting of thieno[3,4-b]pyrazines based low-band gap polymers as hole - transporting materials have shown improved efficiencies. The optimized structures of the studied compounds have been shown in Scheme 3.



C1



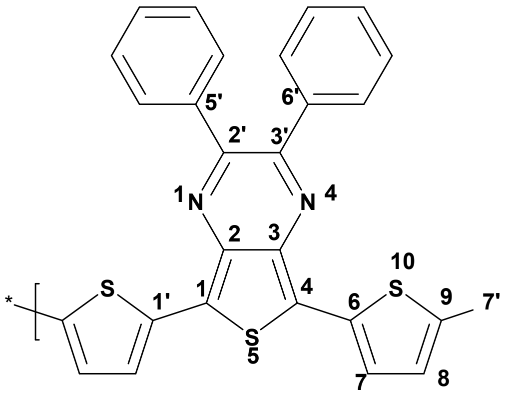
C2



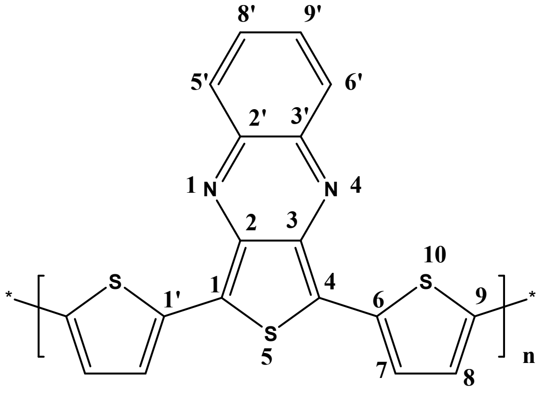
Scheme 3: Structures of the investigated compounds.

4.1. Geometry optimization results

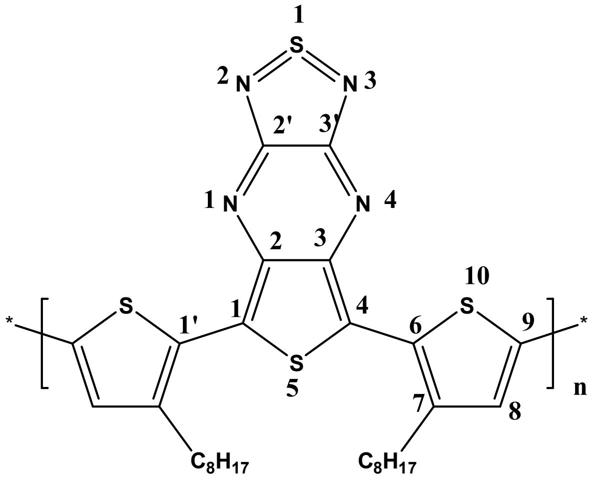
For determining the optimization of the studied compounds the atom labeling of thieno[3,4-b]pyrazines and its derivatives are given in Scheme 4.



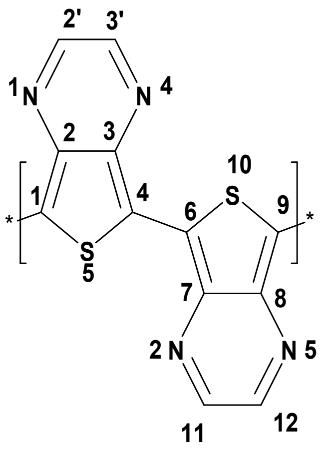
A) **C1-C4**

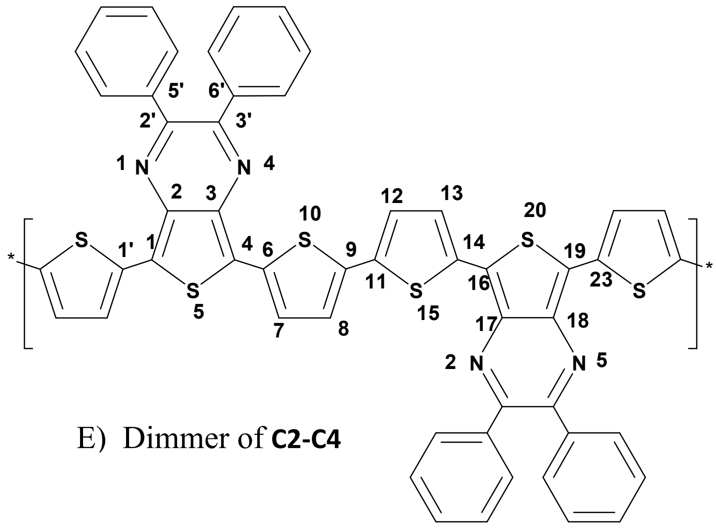


B) **C5**



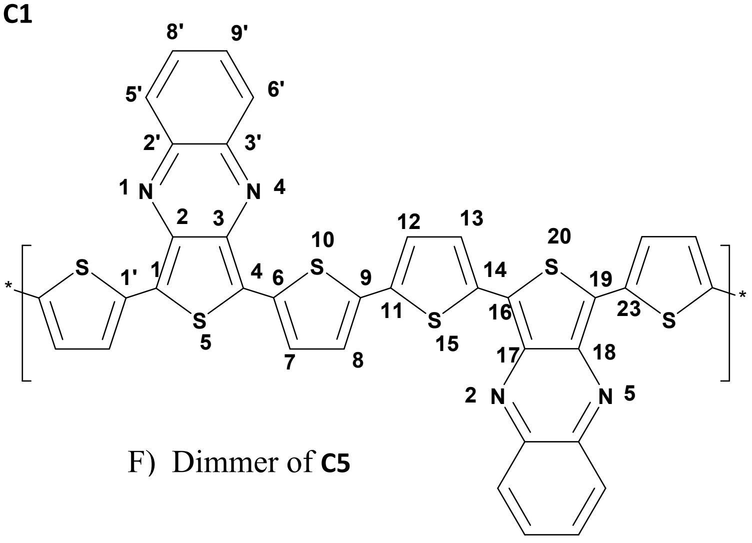
C) **C6**



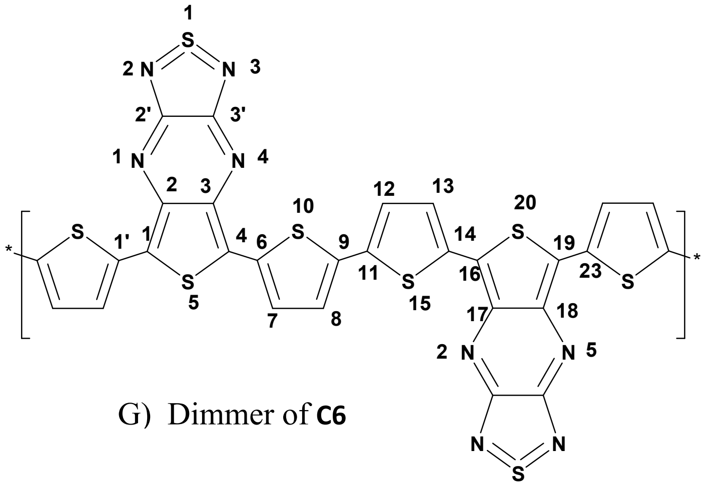


E) Dimmer of **C2-C4**

D) Dimmer of **C1**



F) Dimmer of **C5**



G) Dimmer of **C6**

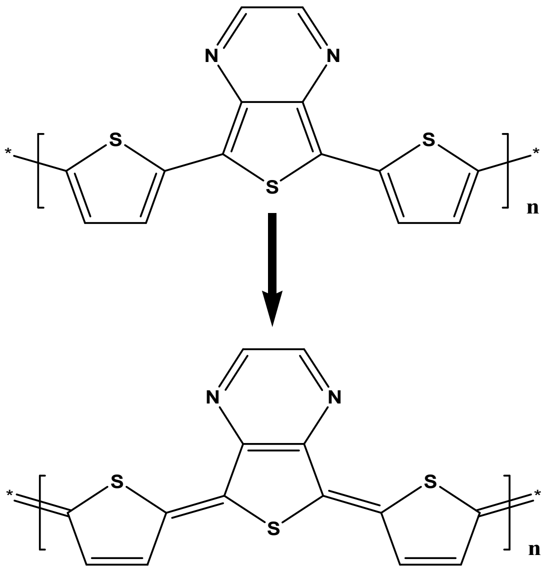
Scheme 4: The atom labeling of investigated compounds.

The calculated structural parameters are given in Tables 1, 2 and 3. It is observed that up on the removal of an electron from the neutral compounds the bond lengths of the oligommers changed. Single bonds become shorter and double bonds become longer in the oxidized structures than the reduced (neutral) structures. This shows that up on oxidation the single bonds show double bond character and the double bonds show single bond character and this implies the emerging of quinoid character of the oligommers.

In all compounds the bond length between $C_{1'}$-C_1, C_2-C_3 and C_4-C_6 [for example in compound **C2** (1.439 to 1.4065 Å), (1.4435 to 1.4175 Å) and (1.439 to 1.4065 Å)] decrease up on the removal of an electron, which indicate that the formation of quinoid character up on oxidation.

In all compounds the inter-rings bonds are longer than normal double bonds but shorter than the single bonds. From these bond lengths it is also possible to confirm the emerging of a quinoidal like distortions as a result of oxidation.

Depending on this evidence the following scheme can explain the formation of quinoidal structures from the aromatic structures.



Scheme 5: Structure of aromatic and quinoid forms of the terthienyl TP.

The C2'- C3' bond in compound (**C3**) and (**C4**) increase compared to other compounds. Due to the steric hindrance between the phenyl and thiophene groups to thieno [3,4-b] pyrazine.

For all studied compounds a thiophene molecules which is fused to pyrazine the adjacent C-S bond length are identical in the reduced form, and this result also observed for the oxidized form since they are in identical chemical environments. While the extreme C-S bond of unsubstituted thiophene is not identical. For example in compound (**C2**) the bond length between $S_{10}C_6$ and C_9S_{10} (1.7612, 1.7333 Å), respectively which shows that they are not identical even if they are in the same environment. due to the steric effect of pyrazine.

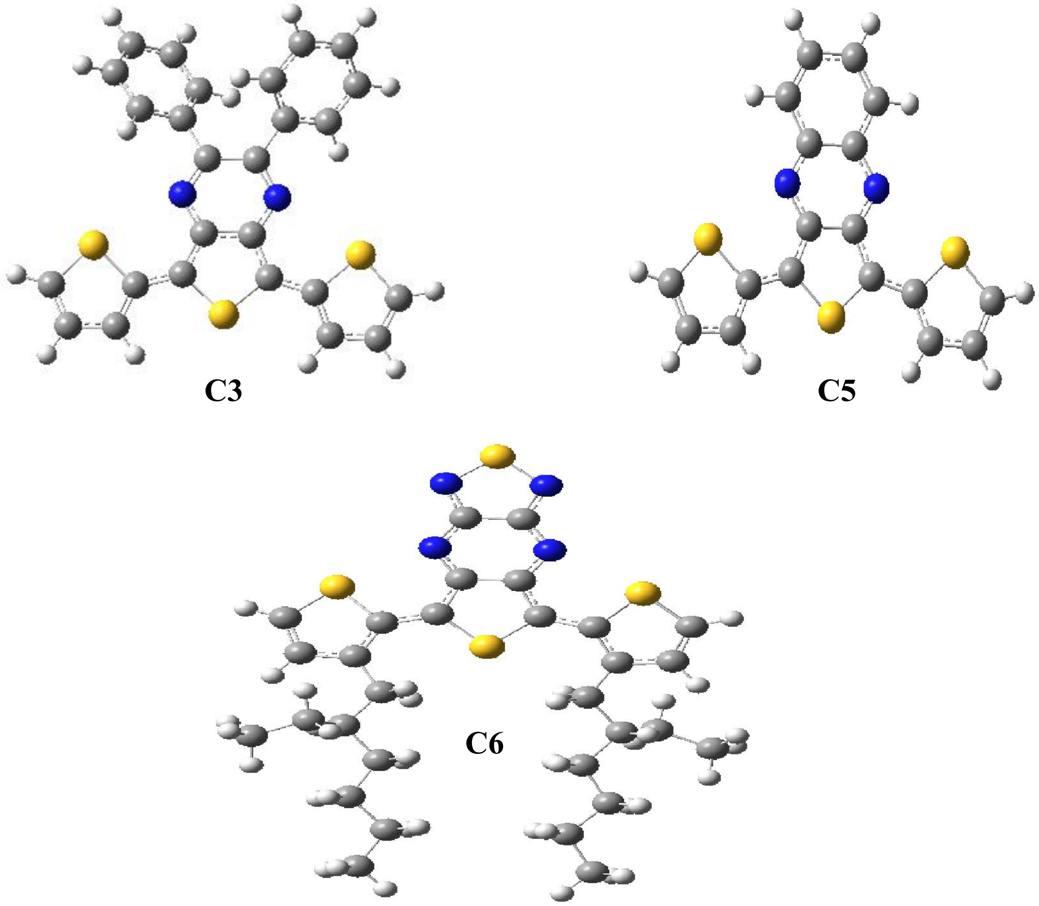


Figure 5: Optimized geometries obtained by B3LYP/6-31G (d) of the selected molecules.

Table 1: Optimized selected bond lengths (in Å) of the studied molecules in neutral (reduced) and polaronic (oxidized) states obtained by B3LYP/6-31G (d) level.

Parameter	Monomer of **C1**		Dimmer of **C1**		Monomer of **C2**		Dimmer of **C2**	
	Red	Oxd	Red	Oxd	Red	Oxd	Red	Oxd
$C_{1'}C_1$	-	-	-	-	1.439	1.4065	1.4378	1.4221
C_1C_2	1.3834	1.4215	1.3832	1.407	1.3978	1.4293	1.3989	1.4182
C_2C_3	1.4526	1.4232	1.4455	1.4214	1.4435	1.4175	1.4422	1.4268
C_3C_4	1.3834	1.4215	1.4029	1.4327	1.3978	1.4293	1.4009	1.415
C_4S_5	1.7181	1.728	1.7472	1.7684	1.7469	1.7546	1.7495	1.7582
S_5C_1	1.7181	1.728	1.7196	1.7106	1.7469	1.7546	1.748	1.7468
C_2N_1	1.3724	1.3456	1.3704	1.3565	1.3645	1.3498	1.364	1.3545
$N_1C_{2'}$	1.3088	1.3298	1.311	1.3189	1.3114	1.3213	1.3122	1.3177
$C_{2'}C_{3'}$	1.4417	1.4276	1.4366	1.4311	1.436	1.4267	1.4346	1.4289
$C_{3'}N_4$	1.3088	1.3298	1.313	1.3234	1.3114	1.3213	1.313	1.3186
N_4C_3	1.3724	1.3456	1.3623	1.3479	1.3645	1.3498	1.3621	1.3555
C_4C_6	-	-	1.4346	1.393	1.439	1.4065	1.4315	1.4081
C_6C_7	-	-	1.4029	1.4327	1.3847	1.4083	1.3891	1.4109
C_7C_8	-	-	1.4455	1.4214	1.4188	1.3977	1.4065	1.3843
C_8C_9	-	-	1.3832	1.407	1.3697	1.3868	1.3866	1.4081
C_9S_{10}	-	-	1.7196	1.7106	1.7333	1.7181	1.7588	1.7643
$S_{10}C_6$	-	-	1.7472	1.7684	1.7612	1.7694	1.7612	1.7612
C_7N_2	-	-	1.3623	1.3479	-	-	-	-
N_2C_{11}	-	-	1.313	1.3234	-	-	-	-
$C_{11}C_{12}$	-	-	1.4366	1.4311	-	-	-	-
$C_{12}N_5$	-	-	1.311	1.3189	-	-	-	-
N_5C_8	-	-	1.3704	1.3565	-	-	-	-
C_9C_{11}	-	-	-	-	-	-	1.4381	1.4107
$C_{14}C_{16}$	-	-	-	-	-	-	1.4315	1.4081
$C_{19}C_{23}$	-	-	-	-	-	-	1.4378	1.4221

Table 2: Optimized selected bond lengths (in Å) of the studied molecules in neutral (reduced) and polaronic (oxidized) states obtained by B3LYP/6-31G (d) level.

Parameter	Monomer of **C3**		Dimmer of **C3**		Monomer of **C4**		Dimmer of **C4**	
	Red	Oxd	Red	Oxd	Red	Oxd	Red	Oxd
$C_{1'}C_1$	1.4384	1.4083	1.4373	1.4234	1.4385	1.4088	1.4373	1.4237
C_1C_2	1.3975	1.4258	1.3984	1.4152	1.3969	1.4248	1.3978	1.4142
C_2C_3	1.4367	1.4137	1.4355	1.4213	1.4365	1.4144	1.4353	1.4216
C_3C_4	1.3975	1.4258	1.4006	1.4147	1.3969	1.4248	1.3998	1.4142
C_4S_5	1.7489	1.7579	1.7515	1.7603	1.7496	1.7587	1.7521	1.761
S_5C_1	1.7489	1.7579	1.7503	1.7495	1.7496	1.7587	1.7508	1.7499
C_2N_1	1.3583	1.3441	1.3582	1.35	1.3584	1.3446	1.3583	1.3504
$N_1C_{2'}$	1.3182	1.3303	1.3188	1.3247	1.3185	1.3308	1.319	1.3249
$C_{2'}C_{3'}$	1.4702	1.4673	1.4689	1.4659	1.4716	1.469	1.4704	1.4677
$C_{3'}N_4$	1.3182	1.3303	1.3197	1.3267	1.3185	1.3308	1.3199	1.3272
N_4C_3	1.3583	1.3441	1.3561	1.3493	1.3584	1.3446	1.3563	1.3496
$C_{2'}C_{5'}$	1.4888	1.4791	1.4889	1.4848	1.4799	1.4677	1.4799	1.4748
$C_{3'}C_{6'}$	1.4888	1.4791	1.4885	1.4839	1.4799	1.4677	1.4793	1.4734
C_4C_6	1.4384	1.4083	1.4308	1.4073	1.4385	1.4088	1.4312	1.4075
C_6C_7	1.3847	1.4057	1.3891	1.4104	1.3846	1.4053	1.3888	1.4101
C_7C_8	1.4191	1.4002	1.4068	1.385	1.4192	1.4007	1.4073	1.3852
C_8C_9	1.3695	1.3844	1.3863	1.4072	1.3694	1.3839	1.3859	1.4068
C_9S_{10}	1.7338	1.7205	1.7591	1.765	1.7339	1.721	1.7588	1.7652
$S_{10}C_6$	1.7615	1.7681	1.7615	1.7617	1.7614	1.7675	1.7615	1.7617
C_9C_{11}	-	-	1.4381	1.4112	-	-	1.4385	1.4113
$C_{14}C_{16}$	-	-	1.4308	1.4073	-	-	1.4312	1.4075
$C_{19}C_{23}$	-	-	1.4373	1.4234	-	-	1.4373	1.4237

Table 3: Optimized selected bond lengths (in Å) of the studied molecules in neutral (reduced) and polaronic (oxidized) states obtained by B3LYP/6-31G (d) level.

Parameter	Monomer of **C5**		Dimmer of **C5**		Monomer of **C6**		Dimmer of **C6**	
	Red	Oxd	Red	Oxd	Red	Oxd	Red	Oxd
$C_{1'}C_{1}$	1.4362	1.4069	1.4346	1.4192	1.4394	1.4068	1.4414	1.4068
$C_{1}C_{2}$	1.4072	1.4336	1.4079	1.4259	1.418	1.4441	1.4128	1.4441
$C_{2}C_{3}$	1.454	1.4348	1.4531	1.4408	1.4753	1.4528	1.473	1.4528
$C_{3}C_{4}$	1.4072	1.4336	1.4117	1.4256	1.418	1.4441	1.4278	1.4441
$C_{4}S_{5}$	1.7408	1.752	1.7446	1.7565	1.7396	1.7544	1.7445	1.7544
$S_{5}C_{1}$	1.7408	1.752	1.7432	1.7453	1.7396	1.7544	1.7428	1.7544
$C_{2}N_{1}$	1.3444	1.3296	1.3442	1.3337	1.3362	1.3236	1.3403	1.3236
$N_{1}C_{2'}$	1.3354	1.3465	1.3364	1.3439	1.3364	1.345	1.3362	1.3450
$C_{2'}C_{3'}$	1.4602	1.4578	1.4589	1.4558	1.4677	1.462	1.4675	1.462
$C_{3'}N_{4}$	1.3354	1.3465	1.3381	1.3464	1.3364	1.345	1.3417	1.345
$N_{4}C_{3}$	1.3444	1.3296	1.3411	1.3327	1.3362	1.3236	1.3297	1.3236
$C_{2'}C_{5'}$	1.4327	1.4231	1.4321	1.4264	-	-	-	-
$C_{3'}C_{6'}$	1.4327	1.4231	1.431	1.4248	-	-	-	-
$C_{5'}C_{8'}$	1.3664	1.3724	1.3669	1.3702	-	-	-	-
$C_{8'}C_{9'}$	1.4334	1.4272	1.4324	1.4282	-	-	-	-
$C_{9'}C_{6'}$	1.3664	1.3724	1.3674	1.3711	-	-	-	-
$C_{4}C_{6}$	1.4362	1.4069	1.4261	1.4019	1.4394	1.4068	1.4241	1.4068
$C_{6}C_{7}$	1.3862	1.407	1.3925	1.4141	1.4022	1.4301	1.4148	1.4301
$C_{7}C_{8}$	1.4181	1.3994	1.4035	1.3817	1.4249	1.4064	1.4047	1.4064
$C_{8}C_{9}$	1.3701	1.3849	1.389	1.4101	1.3672	1.3795	1.39	1.3795
$C_{9}S_{10}$	1.7336	1.7198	1.7602	1.7660	1.7253	1.7141	1.7531	1.7141
$S_{10}C_{6}$	1.7622	1.7684	1.7622	1.7630	1.7698	1.7793	1.7696	1.7793
$C_{2'}\ N_{2}$	-	-	-	-	1.3507	1.3426	1.3509	1.3426
$N_{2}\ S_{1}$	-	-	-	-	1.6309	1.6327	1.6329	1.6327
$S_{1}\ N_{3}$	-	-	-	-	1.6309	1.6327	1.6348	1.6327
$N_{3}\ C_{3'}$	-	-	-	-	1.3507	1.3426	1.3459	1.3426

4.1.1. Comparison with Earlier Theoretical and Experimental Results

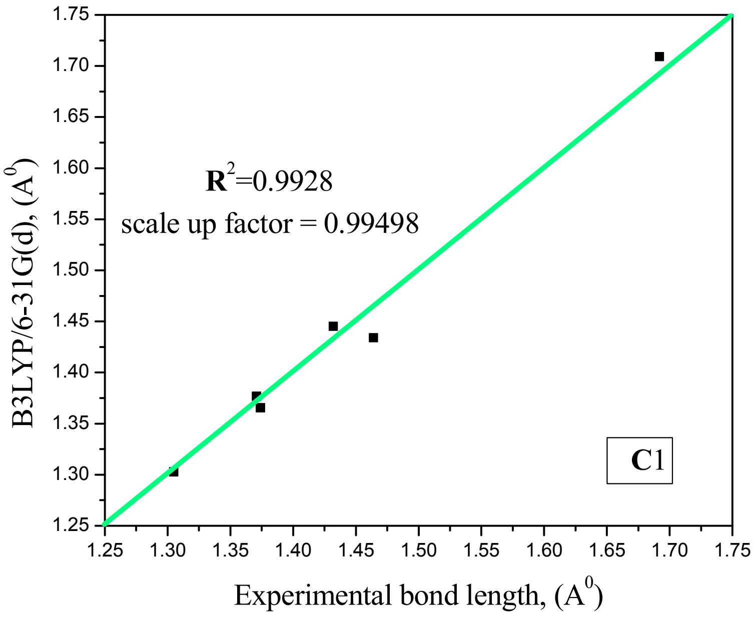
The structural parameters calculated in this work are listed with earlier theoretical and experimental results reported in literatures.

Table 4 : Selected bond length (in Å) of the studied molecules in neutral (reduced) state.

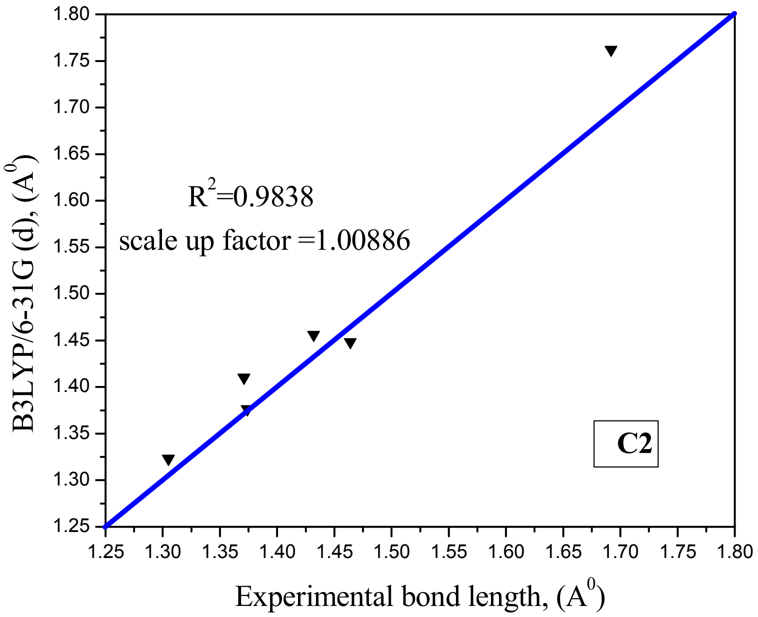
Parameter	C1			C2	
	This work (B3LYP/6-31G(d)	Ref. 63(cal) B3LYP cc-pVDZ	Ref. 60,61 and 62 (Exp)[a]	This work (B3LYP/6-31G(d)	Ref. 63 (cal) B3P86-30% functional CEP-31G*
C_1C_2	1.3834	1.387	1.371	1.3978	1.412
C_2C_3	1.4526	1.453	1.432	1.4435	1.449
C_3C_4	1.3834	1.387	1.371	1.3978	1.412
C_4S_5	1.7181	1.722	1.692	1.7469	1.743
S_5C_1	1.7181	1.722	1.692	1.7469	1.743
C_2N_1	1.3724	1.373	1.374	1.3645	1.365
$N_1C_{2'}$	1.3088	1.311	1.305	1.3114	1.312
$C_{2'}C_{3'}$	1.4417	1.443	1.464	1.436	1.453
$C_{3'}N_4$	1.3088	1.311	1.305	1.3114	1.312
N_4C_3	1.3724	1.373	1.374	1.3645	1.365
C_4C_6	-	-	-	1.439	1.448
C_6C_7	-	-	-	1.3847	1.402
C_7C_8	-	-	-	1.4188	1.421
C_8C_9	-	-	-	1.3697	1.402
C_9S_{10}	-	-	-	1.7333	1.754
$S_{10}C_6$	-	-	-	1.7612	1.754

[a] X-ray data averaged from the structures reported for 2,3-dimethyl -TP (Ref. 60), 2,3 dihexyl -TP (Ref. 61), and 2,3-bis(bromomethyl) -TP (Ref. 62).

Considering C-C, C-N and C-S bond lengths for compound **C1** and **C2**, methods used in this work estimated a satisfactory result with the experimental but the theoretical result reported using B3LYP cc-pVDZ and B3P86-30% functional CEP-31G* are slightly different from the experimental results.



(a)



(b)

Figure 6: Correlation graph between the calculated *verses* the experimental a) for compound **C1** and b) for compound **C2**.

The numbering the carbon and sulfur atoms are based on Scheme 4. Figure 6 shows the correlation relationship between experimental and theoretical bond length in (A^0). The correlation values are found to be 0.9928 and 0.9838 for compound **C1** and **C2**, respectively. Generally from Figure 6 the scaled linear regression data for compound **C1** and **C2** which showed that there was good correlation between the experimental bond length and the computational.

Unfortunately, there is no experimental information about our compound **C6** ([1,2,5]thiadiazolo[3,4-b]thieno[3,4-e]pyrazine), but we can give a good explanation for the geometries. For a compound **C6** the adjacent C-N and N-S bond lengths are identical in the reduced form, and this result is also observed for the oxidized form since they are in identical chemical environments.

Both N_2-S_1 and S_1- N_3 bond length in compound **C6** increase up on the removal of an electron, from 1.6309 Å to 1.6327 Å, while the bond length of both $C_{2'}$-N_2 and N_3- $C_{3'}$ decrease up on the removal of an electron, from 1.3507 Å to 1.3426 Å Up on the removal of electron the bond length is changed this is due to the contribution of hetro atom to the resonance of aromatic ring.

In compound **C6** the bond length between N_1- $C_{2'}$ and $C_{2'}$-$C_{3'}$ (1.3364 Å, 1.4677Å), respectively increased with compare to compound **C2 (**1.3114 Å, 1.436Å), respectively due to introduction of fused thiadiazol to Thieno[3,4-b]pyrazine.

The bond length between $C_{1'}$-C_1, C_2-C_3 and C_4-C_6 in compound **C6** (1.4394 to 1.4068 Å), (1.4753 to 1.4528 Å) and (1.4394 to 1.4068 Å)] decrease up on the removal of an electron, which indicate that the formation of quinoid character up on oxidation.

Compared to compound **C6** and **C5** the bond length between $C_{2'}$-N_2 (1.3507 Å) and $C_{2'}$-$C_{5'}$ (1.4327 Å), respectively increase due to steric effect of (N-H) in compound **C5**.

According to previous AM_1 calculations on the tetramer models of [1,2,5]thiadiazolo[3,4-b]thieno[3,4-e]pyrazine with thiophene (**C6**), s-trans coplanar structures are, in fact, most stable in energy. Similar systems involving thieno[3,4-b]pyrazine also have nearly coplanar X-ray structures. Due to the favorable inter-ring S-N or H-N interactions, where the nitrogen atoms in the pyrazine ring are important to retain the coplanarity. We therefore consider that the coplanar s-trans geometries are reasonable for the one-dimensional systems as in Figure 5 [59].

Table 5: Selected bond length (in Å) of the studied molecules (**C6**) in neutral (reduced) and polaronic (oxidized) states.

Parameter	**C6**		
	This work (B3LYP/6-31G (d) Neutral form	This work (B3LYP/6-31G (d) Polaronic form	Ref.59 (cal) MNDO/PM3 Neutral form
$C_{1'}C_1$	1.4394	1.4068	-
C_1C_2	1.4180	1.4441	1.428
C_2C_3	1.4753	1.4528	1.470
C_3C_4	1.4180	1.4441	1.428
C_4S_5	1.7396	1.7544	1.697
S_5C_1	1.7396	1.7544	1.697
C_2N_1	1.3362	1.3236	1.344
$N_1C_{2'}$	1.3364	1.345	1.376
$C_{2'}$ N_2	1.3507	1.3426	1.352
N_2 S_1	1.6309	1.6327	1.702
S_1 N_3	1.6309	1.6327	1.702
N_3 $C_{3'}$	1.3507	1.3426	1.352
$C_{2'}C_{3'}$	1.4677	1.462	1.470
$C_{3'}N_4$	1.3364	1.345	1.376
N_4C_3	1.3362	1.3236	1.344
C_4C_6	1.4394	1.4068	1.434
C_6C_7	1.4022	1.4301	1.381
C_7C_8	1.4249	1.4064	1.423
C_8C_9	1.3672	1.3795	1.381
C_9S_{10}	1.7253	1.7141	1.739
$S_{10}C_6$	1.7698	1.7793	1.739

4.2. UV-Visible Absorption

The electronic spectra involving transition of valence electrons that occur in the UV-Vis region was studied computationally in order to investigate the optical property and electronic transition. The excitation energy and UV-Vis absorption spectra for the singlet-singlet transition of all compounds were simulated using TD-DFT with B3LYP functional in chloroform solution.

Therefore, from the optimized structure obtained with the method B3LYP/6-31G (d) of each studied compound, we have calculated the vertical excited singlet states, transitions energies and oscillator strength using TD-DFT method. As illustrated in Table 6, we can find the values of calculated absorption λ_{max} (nm) and oscillator strength (O.S) along with main excitation configuration of the studied compounds.

Table 6 : Absorption wavelength λ_{abs} (nm), excitation energies and oscillator strengths obtained by the TD-DFT method.

Comp-ound	Excitation States	λ_{abs} (nm)	E_{ex} (nm)	O.S (f) a.u	MO/character	coefficient
C1	1	377.09	377.14	0.0029	HOMO-1→LUMO	0.70470
	2	359.31	359.35	0.0437	HOMO→LUMO	0.69637
	3	279.41	279.44	0.2562	HOMO-3 →LUMO	0.66901
C2	1	614.09	614.16	0.3288	HOMO→LUMO	0.70177
	2	390.35	390.40	0.0016	HOMO-4→LUMO	0.69755
	3	362.53	362.57	0.0133	HOMO-1→LUMO	0.65900
C3	1	623.67	623.74	0.2581	HOMO→LUMO	0.70240
	2	408.51	408.56	0.1972	HOMO-1→LUMO	0.65921
	3	393.66	393.71	0.0016	HOMO-3→LUMO	0.67587
C4	1	618.94	619.00	0.2600	HOMO→LUMO	0.70238
	2	431.24	431.28	0.1969	HOMO-1→LUMO	0.66351
	3	389.49	389.53	0.0016	HOMO-4 →LUMO	0.56614
C5	1	830.81	830.93	0.1924	HOMO→LUMO	0.70710
	2	443.16	443.22	0.0009	HOMO-4 →LUMO	0.70205
	3	406.21	406.26	0.0593	HOMO-1→LUMO	0.67724

C6	1	1509.74	1509.9	0.0613	HOMO → LUMO	0.71620
	2	521.63	521.70	0.0004	HOMO-4 → LUMO	0.59176
	3	494.42	494.49	0.0520	HOMO-1 → LUMO	0.59953

From Table 6, compounds **C2**, **C3** and **C7** exhibit a strong absorption band in the visible region around 614 – 684 nm, and for the compound **C5** and **C6** they are out of Uv-vis region due to the fused system and the hetro atom effect.

From Table 6 it is observed that the compound **C1** is absorbing at a shorter wavelength range and it shows that it is colorless, while other compounds except **C5** and **C6** the absorption wavelength increases to the visible range, which indicates they are colored.

With increase in the chain length, the excitation energy decreases, implying ease of removing electrons upon polymerization.

In compounds **C5** and **C6** the excitation energy is very small as compared to others which indicate the ease of removing electrons.

In all compounds two peaks were obtained from lowest singlet electronic excitation is characterized π - π* transition while the long-wavelength absorption peaks can be attributed to intramolecular charge transfer between the thiophene donor and the acceptor moieties.

Excitation state one ($S_0 \rightarrow S_1$) corresponds almost exclusively the promotion of an electron from the HOMO to LUMO orbital except compound **C1**.

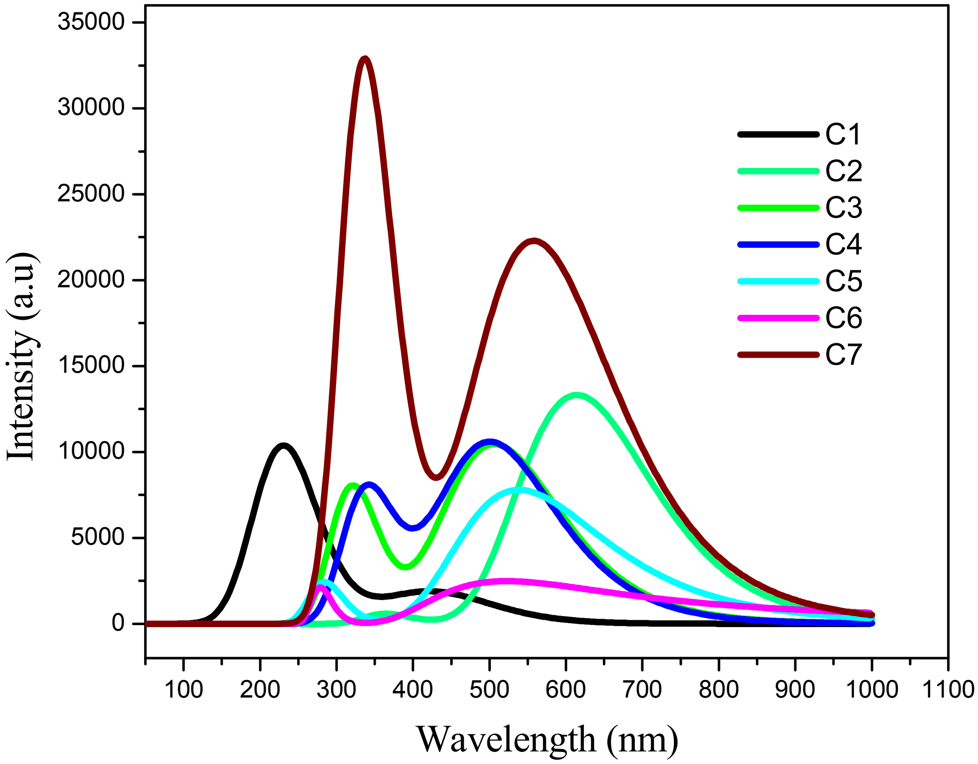


Figure 7: Simulated Uv-Vis absorption spectra of the investigated compounds in CCl_4 solvent.

The absorption wavelengths arising from ($S_0 \rightarrow S_1$) electronic transition increase progressively with the increase of conjugation lengths (i.e. **C1 < C2 < C4 < C3**) which shows that the decrease of LUMO and increase of HOMO energy. A good photovoltaic material should have broad and strong visible absorption characteristics.

4.3. Band Gaps

The band gaps of the thieno[3,4-b]pyrazines and its derivatives are calculated using DFT/B3LYP/6-31G(d) levels of theory. The band gap is obtained by subtracting the energy of the lowest unoccupied molecular orbital (LUMO) from the energy of the highest occupied molecular orbital (HOMO) i.e. E_{LUMO} - E_{HOMO}.

Table 7 : The theoretical electronic properties (HOMO, LUMO and Eg) of thieno[3,4-b]pyrazines and its derivatives calculated by B3LYP/6-31G (d).

Compounds	Neutral form			Polaronic form		
	E_{HOMO} (ev)	E_{LUMO} (ev)	Eg	E_{HOMO} (ev)	E_{LUMO} (ev)	Eg
C1	-6.2377	-2.2653	**3.9724**	-12.0354	-8.1316	**3.9038**
Dimmer of **C1**	-5.3421	-2.7728	**2.5693**	-9.7629	-7.1471	**2.6158**
C2	-5.0033	-2.6242	**2.3791**	-8.9142	-6.6502	**2.264**
Dimmer of **C2**	-4.6398	-2.8599	**1.7799**	-7.2810	-5.6287	**1.6523**
C3	-4.8828	-2.5426	**2.3402**	-8.4734	-6.1827	**2.2907**
Dimmer of **C3**	-4.5222	-2.7551	**1.7671**	-6.9569	-5.2967	**1.6602**
C4	-4.9135	-2.5606	**2.3529**	-8.4755	-6.1715	**2.304**
Dimmer of **C4**	-4.5756	-2.7842	**1.7914**	-6.9846	-5.3146	**1.67**
C5	-4.7955	-2.9690	**1.8265**	-8.5321	-6.6997	**1.8324**
Dimmer of **C5**	-4.4447	-3.1448	**1.2999**	-6.9743	-5.7277	**1.2466**
C6	-4.8164	-3.5739	**1.2425**	-8.3603	-6.9377	**1.4226**
Dimmer of **C6**	-4.5201	-3.7154	**0.8047**	-6.9132	-5.8284	**1.0848**

From Table 7 it is observed that the calculated band gap Eg of the studied model compounds increases in the following order **C6** < **C5** < **C3** < **C4** < **C2** < **C1**. The much lower Eg of **C5** and **C6** is observed due to the fused ring system, while we compare to compound **C6** and compound **C5**, Compound **C6** has smaller band gap because of the hetro atom effect of N and S.

Adding of aliphatic groups in **C6** has insignificant effect on electronic property (band gap) of the compounds. Rather it affects the solubility of the polymer.

For **C6** the three rings in the terthienyl TP units are almost coplanar, which is preferable for the band gap reduction of π -conjugated systems.

In compound three (**C3**) and four (**C4**) the bond length between C1'- C1 have a length of about 1.4384, 1.4385 Å, respectively while the C1- C2 have a length of about 1.3975, 1.3969 Å, respectively Based on these bond distances the bond length alternation (BLA) can be quantified taking $\Delta R_{BLA} = R(C_{1'}C_{1}) - R(C_{1}C_{2})$ as measures of the BLA take values of 0.0409 and 0.0416 Å, respectively which indicate that compound **C3** has better band gap than compound **C4.**

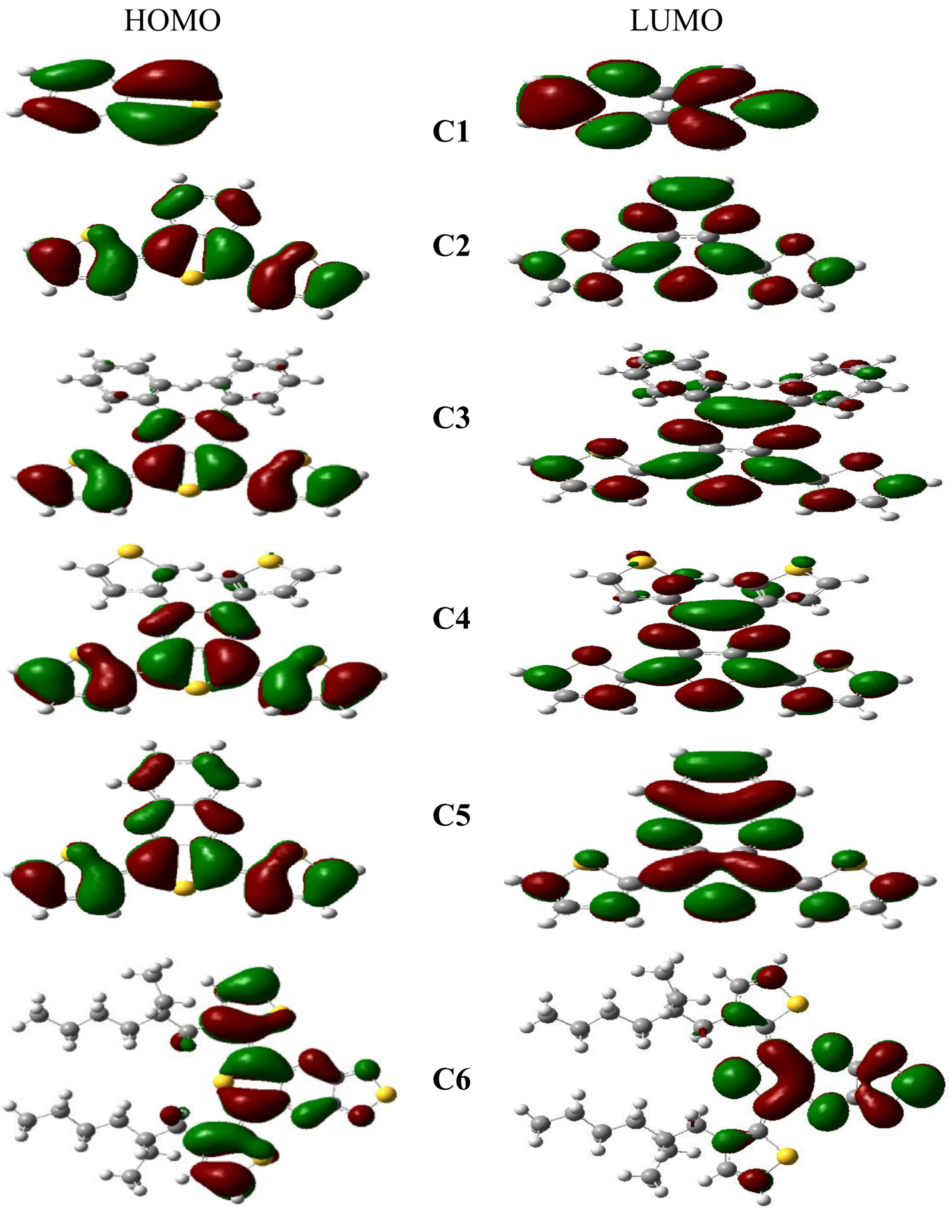


Figure 8: The contour plots of HOMO and LUMO orbital of the studied compounds.

4.4. Thermodynamic Properties

The stability of the studied polymer at the oxidized states by using DFT/B3LYP/6-31G(d) calculations were carried out for all the compounds and the Gibbs free energy, enthalpy and entropy of the compounds are determined. The change in the thermodynamic properties is calculated by subtracting the thermodynamic properties of the reduced compounds from the thermodynamic properties of the oxidized compounds. The results are listed in Table 8.

Table 8 : Thermodynamic properties of thieno[3,4-b]pyrazines and its derivatives calculated by B3LYP/6-31G (d).

Compounds	$\Delta G^0 (kcal/mol)$	$\Delta H^0 (kcal/mol)$	$\Delta S^0 (cal/mol.K)$
C1	-0.2963	-0.2983	-2.547
C2	-0.231	-0.231	0.417
C3	-0.222	-0.221	0.47
C4	-0.222	-0.222	0.364
C5	-0.221	-0.221	0.224
C6	-0.219	-0.218	2.555

The result obtained from Table 8, showed that all the studied compounds have similar thermodynamic properties except compound **C1** which indicate that up on polymerization the change in thermodynamic properties decreases.

This decrease in change in thermodynamic properties shows that the oxidized forms of the compound **(C1)** is unstable compared to other compounds.

The conjugation length increases the stability of the oxidized species for all cases. For example compound two (**C2**) has a change in Gibbs free energy of -0.231kcal/mol, which is less than compound one (**C1**) with a change in Gibbs free energy of -0.2963 kcal/mol that supports the stability of the radical cation of compound (**C2**).

Chapter 5 Conclusions

In this study, theoretical analysis on the geometries and electronic properties of seven various compounds based on Thieno [3,4-b]pyrazines in order to display the effect of substituted groups a on the structural and optoelectronic properties of these materials were made.

The following conclusions were drawn:

- During the doping process and for all studied compounds the single bonds become shorter while multiple ones become longer. The inter ring bonds are longer than normal double bonds. This confirms the emerging of a quinoidal like distortions as a result of oxidation.
- The results of the optimized structures for all studied compounds showed that they have similar conformations except compound **C5** and **C6**.
- The HOMO level, LUMO level, and band gap of the studied compounds were well controlled by the acceptor strength. The calculated band gap (E_{gap}) of the monomer was in the range of 1.2425 - 3.9724 eV.
- Compound **C5** and **C6** have better band gap polymers but the absorption wave length is out of uv-vis region due to fused system and hetro atom effects.
- The UV–Vis absorption properties have been obtained by using TD/ B3LYP calculations. The obtained absorption maximums are in the range of 614 – 684 nm for compounds **C2**, **C3** and **C4**.
- The result obtained from thermodynamic properties showed that all the studied compounds have similar properties except compound one (**C1**) which indicate that up on polymerization the change in thermodynamic properties decreases showed that the oxidized forms of the compound **(C1)** is unstable.

The theoretical results suggest that both the acceptor strength and the stable geometry contribute significantly to the electronic properties of alternating donor – acceptor conjugated copolymers. Finally, the procedures of theoretical calculations can be employed to predict the electronic properties on the other compounds, and further to design novel materials for organic solar cells.

References

1. F. Jensen, *Introduction to Computational Chemistry*, John Wiley & Sons, Ltd, (**1999**).

2. M. R. Mueller, *Fundamentals of Quantum Chemistry*: Molecular Spectroscopy and Modern Electronic Structure Computations, Kluwer Academic Publishers, (**2002**).

3. J. K. Labanowski, Simplified and Biased Introduction to Density Functional Approaches in Chemistry see: http://www.ccl.net/cca/documents/DFT/dftoverview/dft2.pdf Accessed 11:46-4/13/2014

4. W. B. Smith, *Introduction to Theoretical Organic Chemistry and Molecular Modeling*, Wiley-VCH, Inc, (**1996**).

5. I. N. Levine, *Quantum Chemistry*, 4th ed, Prentice Hall: Engelwood Cliffs, NJ, (**1991**).

6. D. A. McQuarrie, *Quantum Chemistry*, Viva Books P. L. C, New Delhi, (**2005**).

7. J. B. Foresman, Frisch, Exploring Chemistry with Electronic Structure.

8. T. Clark, *A Handbook of Computational Chemistry*, John Wiley & Sons, Inc, (**1985**).

9. G. Odian, *Principles of Polymerization 3rd ed*, Wiley-Interscience publication, (**1993**), p.1.

10. A. F. Diaz, K. K. Kanazawa and G. P. Gardini, *J. Chem. Soc,Chem. Commun, (*(**1979**) 635.

11. A. R. Hepburn, J. M. Maud and J. M. Marshall, *Met.Mater. (Inst. Mater*). 7 (**1991**) 747.

12. T. J. Yamamoto, J. Chem. Soc. Chem. Commun. (**1981**) 187.

13. K. S. V. Santhanam and N. Gupta. TRIP1. (**1993**) 284.

14. M. Mastragostino, A. M. Marinangeli, A .Corradini and S. Giacobbe, *Synth.Met.* 28 (**1989**) C501.

15. S. Panero, S. Passerini and B. Scrosati, *Mol. Cryst. Liq. Cryst*. 229 (**1993**) 97.

16. J. C. Dubois, *Synth. Met.* 28 (**1989)** C871.

17. J. Roncali, R. Garreau, D. Delabouglise, F. Garnier and M. Lemaire, *J.Chem.Soc.Chem. Commun. (***1989)** 679.

18. W. R. Salaneck, Science and applications of conducting polymers, Proc of the 6th Euro physics industrial workshop, Adam Hilger. (**1991).**

19. D. D. C. Bradley, *Chem. Ber*. 8 (**1991)** 719.

20. K. Davidson, *Educ. Chem*. 28 (**1991)** 155.

21. A. F. Diaz, *J. Electrochem. Soc*. 123 (**1989)** 115.

22. R. J. Waltman, *Can. J. Chem*. 64 (**1986)** 76.

23. G. Tourillon and F. Garnier, *J. Electroanal. Chem*. 135 (**1982)** 173.

24. R. J. Waltman, J. Bargon and A. F. Diaz, *J. Phys. Chem*. 87 (**1983)** 1459.

25. T. Yamamoto, K. Sanechika and A. Yamamoto, *J. Polym. Sci. Polym. Lett. Ed*. 18 (1980) 9.

26. G. Tourillon and F. Garnier, *J. Electrochem. Soc*. 130 (**1983)** 2042.

27. S. Glenis, D. S. Ginley and A. J. Frank, *J. Appl. Phys*. 62 (**1987)** 190.

28. Salzner, U. Lagowski, J. B. Pickup, P. G and Poirier, *A Synth.Met.* 96 (**1998)** 177

29. T. A Skotheim, Ed. *Hand book of conducting polymers*, Marcel Dekker: New York, (**1986**) p. 294.

30. Yamamoto, T. Progr, *Polym.Sci.* 17 (**1992)** 1153.

31. J. Roncali, *J.Chem. Rev*. 92 (1992) 711.

32. Salzner, U. Lagowski, J. B. Pickup, P. G and Poirier, *J. Comp. Chem*. 18, 15 **(1997)** 1943.

33. Salzner, U. Lagowski, J. B. Pickup, P. G. and Poirier, *A. Synth. Met*. 98 (**1999**) 221.

34. Y. Ito, H. Shirakawa and S. Ikeda, *J. Polym. Sci*. 13 (**1975)** 1943.

35. P. Kovacic and A. Kyriakis, *J. Am.Chem.Soc*. 85 **(1963)** 454.

36. R. B. Kaner, Electrochemical Science and Technology of Polymers, *Elsevier Applied Science*. 97 (**1990).**

37. E. M. Genies, G. Bidan and A. F. Diaz, *J.Eletroanal.Chem.* 149 (**1983)** 101.

38. G. P. Evans, Advances in Electrochemical Science and Engineering, Vol.1, Cambridge Life Science, Cambridge, (**1990).**

39. J. Hornback, *Organic chemistry*. 2nd Edi. Belmont, USA: Brooks/cole. (**2006)**.

40. I. Fernandez and G. Frenking. π-Conjugation in donor-substitute cyanoethynlethenes: an EDA study*, Chem.Commun*. **(2006)** 5030.

41. E. Taylor.Ed. The chemistry of Heterocyclic Compounds. New York: Wiley. (**1993)**.

42. C. Wong. Ed. Polymers for electronic and photonic applications. Boston MA: Academic. (**1993**).

43. A. Jahnke, G. Howe, and D. Seferos. Polytellurophenes with Properties Controlled by Tellurium-Coordination. *Angew. Chem. Int. Ed*. 49 **(2010**) 1.

44. T. Baumgartner. Pi-conjugated heterocyclic fused bithiophene materials, *J. Inorg. Organomet. Poly. Mater*. 15 (**2006**) 389.

45. M. Hissler, P. Dyer and R. Reau. Linear organic π-conjugated systems featuring the heavy group 14 and 15 elements. Coordination chemistry Reviews. 244 (**2003**) 1.

46. B. Streetman and S. Banerjee. Solid state electronic devices. 6th Edition.Upper Saddle River, NJ: Prentice Hall (**2000**).

47. J. Roncali, Molecular engineering of the band gap of π-conjugated systems: Facing Technological Applications, *Macromol.Rapid.Commun*, 28 (**2007**) 1761.

48. Brocks, G. Tol, *A. J. Phys. Chem*. 100 (**1996)** 1838.

49. Ajayaghosh, *A. Chem Soc. Rev*. 32 (**2003)** 181.

50. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, J. K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J.

Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, , J. V. Ortiz, Q. Cui, A. G. Baboul, S.Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al- Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, GAUSSIAN 09, Revision B.04, Gaussian, Inc., Pittsburgh PA, (**2003**).

51. J. B. Foresman, E. Frisch, Exploring Chemistry with Electronic Structure Methods; *Gaussian Inc: Pittsburgh*. (**1993)**.

52. T. Liu, J. S. Gao, B. H. Xia, X. Zhou, H. X. Zhang, *Polymer.* 48 (**2007**) 502.

53. L. Yang, J. K. Feng, A. M. Ren, J. Z. Sun, *Polymer*. 47 (**2006**) 1397.

54. G. J. Zhao, G. L.Wu, C. He. F. Q. Bai, H. X. Xi, H. X. Zhang, Y. F. Li, *J. Phys. Chem.C* . 113 (**2009**) 2636.

55. F. Zhang, E. Perzon, X. Wang, W. Mammo, M. R. Anderson, O. Inganas, *Adv. Funct.Mater*. 15 (**2005)**, 745.

56. M. M. Wienk, R. Turbiez, M. P. Struijk, M. Fonrodona, R. A. Janssen, *J. Appl. Phys. Lett.* 88 (**2006)** 153511.

57. X. Wang, E. Perzon, F. F. Langa, S. Admassie, M. R. Anderson, O. Inganas, Adv. Funct. Mater. 15 (**2005)** 1665.

58. K. R. J. Thomas, J. T. Lin, Y. T. Tao, *C. H.* Chuen, *Adv.Mater*. 14 (**2002)** 822.

59. M. Tachibana, S. Tanaka, Y. Yamashita and K. Yoshizawa, *J. Phys. Chem. B.* 106 (**2002**) 3549.

60. D. D. Kenning, K. A. Mitchell, T. R. Calhoun, M. R. Funfar, D. J. Sattler, and S. C. Rasmussen, *J. Org. Chem*. 67 (**2002**) 9073.

61. L. Wen, B. C. Duck, P. C. Dastoor, and S. C. Rasmussen, *Macromolecules* 41 (**2008**) 4576.

62. L. Wen, J. P. Nietfeld, C. M. Amb, and S. C. Rasmussen, *J. Org. Chem*. 73 (**2008**) 8529.

63. C. Kitamura, S. Tanaka and Y. Yamashita, *J. Chem. Soc. Chem. Commun*. (**1994**) 1585.