A DFT STUDY ON THE EFFECT OF ELECTRON DONOR AND ACCEPTOR SUBSTITUTION ON QUINOLINE RING

Project Report Submitted To

MAHATMA GANDHI UNIVERSITY

In Partial Fulfilment of the Requirement for the Degree of
Master of
Science in Chemistry

Submitted By

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CERTIFICATE

I certify that this is the bona fide record of the project work entitled **" A DFT STUDY ON THE EFFECT OF ELECTRON DONOR AND ACCEPTOR SUBSTITUTION ON QUINOLINE RING"** carried out by **ANU VARGHESE Reg. No.200011010678,** under the guidance in partial fulfilment of the requirement for the Degree of Master of Science in chemistry of Mahatma Gandhi University.

Forwarded by,
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DECLARATION

I, **ANU VARGHESE,** do hereby declare that this project work entitled as **" A DFT STUDY ON THE EFFECT OF ELECTRON DONOR AND ACCEPTOR SUBSTITUTION ON QUINOLINE RING",** is exclusively a bonafide work done under the guidance of **Dr. RAJEEV T ULAHANNAN**, Department of physics, Pavanatma college , murickassery. I further declare that no part of this project has previously formed on the basis for the award of any degree , diploma and fellowship or any other similar title of recognition of any other university or similar institution.

MURICKASERRY

DATE ANU VARGHESE

ACKNOWLEDGEMENT

First of all, I express my heartfelt gratitude to the Lord Almighty for strengthening me to work hard and for the endless blessing showered on me throughout my project work. I also express my sincere thanks to Rev. Dr BENNICHEN SCARIA, principal of our college for providing the required facilities.

I also thank our Head of the department of chemistry, Mr. SAJI K JOSE ,for providing all the necessary support required for the completion of this project. I wish to extend my sincere thanks and indebtness to my guide Dr. RAJEEV T ULAHANNAN Department of physics, Pavanatma college for the unshakable support and guidance throughout the work.

I also wish to extend my thanks to all the other teachers and lab assistants of Dept. of chemistry, Pavanatma college, for their corporation during the work . Once again, I wish to extend my sincere thanks to all of the friends, family and teachers for their valuable support and care all the along the journey.

Murickassery ,

DATE   ANU VARGHESE

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CHAPTER 1

INTRODUCTION

1.1) COMPUTATIONAL CHEMISTRY

Computational chemistry is a branch of chemistry that uses computer simulations to assist in solving chemical problems. It uses methods of theoretical chemistry, incorporated into efficient computer programmes, to calculate the structures and properties of molecules and solids. These are also called molecular modeling, is a set of technique for investigating chemical problems using a computer or application of computational methods and algorithms in chemistry. Thus computational chemistry is concerned with performing computer calculation and simultaneous for solving problems in physics and chemistry especially in the area of molecules. It is different from theoretical chemistry. Computational chemistry methods range from very approximate to highly accurate. Computational chemistry uses mathematical methods that are well developed. These methods are automated as computer programs. In theoretical chemistry, chemists, physicists and mathematicians develop algorithm and computers programs to predict atomic and molecular properties and reactions paths for chemical reactions. Computational chemists, in contrast may simply apply existing computer programs and methodologies to answer specific chemical questions .

Definition of computational chemistry

These are two different aspects to computational chemistry

- Computational studies can be carried out to find a starting point for a laboratory synthesis, or to assist in understanding experimental data, such as the position and source of spectroscopic peaks.
- Computational studies can be used to predict the possibility of molecules not yet discovered or to explore reaction mechanism that are difficult to study in chemical experiment.

So, computational chemistry can assist experimental chemists. It also can challenge experimental chemists to find entirely new chemical objects.

Computational chemistry has five major parts,

- The prediction molecule structure by the use of the simulation of forces, or more accurate quantum chemical methods, to find stationary points on the energy surface as the position of the nuclei are varied.
- Computational approaches to help in the efficient synthesis of compounds.
- Computational approaches to design molecules that interact in specific ways with other molecules (for example, drug design and catalysis). Storing and searching for data on chemical entities.
- Identifying correlations between chemical structures and properties.
- Storing and searching for data on chemical entities

1.2) HISTORY

Building on the founding discoveries and theories in the history of quantum mechanics, the first theoretical calculations in chemistry were those of Walter Heitler and Fritz London in 1927. The books that were influential in the early development of computational quantum chemistry include Linus Pauling and E. Bright Wilsons's 1935 Introduction to Quantum Mechanics – with Applications to Chemistry, Eyring, Walter and Kimball's 1944 Quantum Chemistry, Heitler's 1945 Elementary Wave Mechanics – with Applications to Quantum Chemistry, and later Coulsons’s 1952 textbook Valence, each of which served as primary references for chemists in the decades to follow.

The development of efficient computer technology in the 1940s made calculating elaborate wave equation for complex atomic. In the early 1950s, the first semi-empirical atomic orbital calculations were performed. Theoretical chemists became extensive users of the early digital computers. One major advance came with the 1951 paper in Reviews of Modern Physics by Clemens C. J. Roothaan in 1951, largely on the "LCAO - MO" approach (Linear Combination of Atomic Orbitals Molecular Orbitals), for many years the second-most cited paper in that journal. A very detailed account of such use in the United Kingdom is given by Smith and Sutcliffe. The first ab initio Hartree-fock orbitals calculations on diatomic molecules were performed in 1956 at MIT, using a basis set of Slater orbital. For diatomic molecules, a systematic study using a minimum basis set and the first calculation with a larger basis set were published by Ransil and Nesbet respectively in 1960. The first polyatomic calculations using Gaussian orbitals were performed in the late 1950s. The first configurational interactions calculations were performed in Cambridge on the EDSAC computer in the 1950s using

Gaussian orbitals by Boys and co-workers. By 1971, when a bibliography of ab initio calculations was published, the largest molecules included were naphthalene and azulene. Abstracts of many earlier developments in ab initio theory have been published by Schaefer .

In 1964, Huckel method calculations (using a simple Linear combination of atomic orbitals (LCAO) method to determine electron energies of molecular orbitals of π electrons in conjugated hydrocarbon systems) of molecules, ranging in complexity from butadiene and benzene to ovalene, were generated on computers at Berkeley and Oxford. These empirical methods were replaced in the 1960s by semi empirical method such as CNDO.

In the early 1970s, efficient *ab* initio computer programs such as ATMOL, Gaussian, IBMOL, and POLYATOM, began to be used to speed ab initio calculations of molecular orbitals. Of these four programs, only Gaussian, now vastly expanded, is still in use, but many other programs are now in use. At the same time, the methods of molecular mechanics, such as MM2 force field, were developed, primarily by Norman Allinger.

One of the first mentions of the term computational chemistry can be found in the 1970 book Computers and Their Role in the Physical Sciences by Sidney Fernbach and Abraham Haskell Taub, where they state "It seems, therefore, that 'computational chemistry' can finally be more and more of a reality. During the 1970s, widely different methods began to be seen as part of a new emerging discipline of computational chemistry. The journal of computational chemistry was first published in 1980.

Computational chemistry has featured in several Nobel Prize awards, most notably in 1998 and 2013.Walter Kohn, "for his development of the density-functional theory", and John Pople, "for his development of computational methods in quantum chemistry", received the 1998 Nobel Prize in Chemistry. Martin Karplus, Michael Levitt and Ariel Warshel received the 2013 Nobel Prize in Chemistry for "the development of multiscale models for complex chemical systems".

The most important computer soft ware’s used for computational chemistry include,

Abalone, Ball, Dalton, GAMESS,HARTON, AMPAC,Exc code, Gaussian, Jaguar, Avogadro, CASINO, Firefly, GHEMICAL, Khimera, MOLICAS, Nwchem, ONETEP, PARSEC, Q-Chem, Rubychem, Spartan, YAMBO Code .

Using computational chemistry software we can in particular perform

- Electronic structure determination
- Geometry optimization
- Frequency calculation
- Definition of transition structure and reaction paths
- Protein calculation
- Electron and charge distribution calculations
- Calculation of potential energy surfaces
- Calculation of rate constant for chemical reactions
- Thermodynamic calculations-heat of reaction, energy of activation

1.3) FIELDS OF APPLICATION

- Computational studies can be carried out to find a starting point for a laboratory synthesis, or to assist in understanding experimental data, such as the position and source of spectroscopic peaks.
- Computational studies can be used to predict the possibility of so far entirely unknown molecules or to explore reaction mechanisms that are not readily studied by experimental means.
- Thus computational chemistry can assist the experimental chemist or it can challenge the experimental chemist to find entirely new chemical objects.
- Several major areas may be distinguished within computational chemistry.
- The prediction of the molecular structure of molecules by the use of the simulation of forces, or more accurate quantum chemical methods, to find stationary points on the energy surface as the position of the nuclei is varied.
- Storing and searching for data on chemical entities.
- Identifying correlations between chemical structures and properties.
- Computational approaches to help in the efficient synthesis of compounds.
- Computational approaches to design molecules that interact in specific ways with other molecules (eg : drug design and catalysis).

1.4) TOOLS OF COMPUTATIONAL CHEMISTRY

i. Ab- Initio calculations

Ab-Initio a Latin word means from the first principle – calculations are based on the Schrodinger wave equation which describes how the electrons in atoms and molecules behave. The Ab- Initio method solves the Schrodinger equation for a molecule and gives as an energy (E) and wave function (Ψ) of the molecule. The wave function (Ψ) is a mathematical function that can be used to calculate the electron distribution. From the electron distribution, we can identify the polar nature of molecule and electrophilic and nucleophilic cytes etc .

Ab- Initio is useful in calculating the molecular geometries, energies, vibrational frequencies, spectra, ionization potentials, electron affinities etc. The simplest kin of Ab- Initio calculation is Hartree- Fock method. Ab-Initio calculation is slow. It can deals with systems having ≈100 atoms.

Features:

- Uses quantum physics.
- Mathematically rigorous, no empirical parameter.
- Uses approximation extensively.

Advantages:

- Useful for a broad range of systems.
- Does not depend on experimental data.
- Capable of calculating transition states and excited states.

Disadvantages:

- Computationally expensive.

Best for:

- Small systems (tens of atoms).
- System involving electronic transitions.
- Molecules or systems without available experimental data (“new” chemistry).
- Systems requiring rigorous accuracy.

ii. Semi-Empirical calculations [SE calculations]

SE calculations based on Schrodinger – wave equation. However more approximations are made in solving it, and the very complicated Integrals (that must be calculated in the Ab-

Initio are not actually evaluated in the method. Instead the program consist a kind of “library of integrals”) that are combined to the experimental value. This plugging of the experimental values into mathematical procedures to get the best calculated values is called parameterization.

It is a mix of theory and experiment that makes this method Semi-Empirical. SE calculations are much faster than Ab-Initio and DFT calculations. But slower than Molecular Mechanics. It deals with ≈10000 atoms containing big systems.

Features:

- Uses quantum physics.
- Uses experimentally derived empirical parameters.
- Uses approximation extensively.

Advantages:

- Less demanding computationally than Ab-Initio method.
- Capable of calculating transition states and excited states.

Disadvantages:

- Requires experimental data (or data from ab-initio for parameters).
- Less rigorous than (ab-initio) methods.

Best for:

- Medium sized systems (hundreds of atoms).
- Systems involving electronic transitions.

iii. Molecular Mechanics

It is based on a model of molecular as a collection of balls held together by springs. The balls for atoms and the springs are bond between them, and the Energy needed to stretch and bend the springs is evaluated. We can calculate the energy of a given collection of a balls and springs ie, for a given molecule.

Now we can change the geometry until the lowest energy is found. Thus enable us to do the geometry optimization ie, to calculate the geometry of the molecule. Molecular Mechanics is a very fast method and fairly large molecules like steroids or cholesterol can be optimized in seconds. It can deals with systems having 1 lakh Atoms .

Features:

- Uses classical physics.
- Relies on force field with embedded parameters.

Advantages:

- Can be used for molecules as large as enzymes.
- Computationally least intensive fast and useful with limited computer resources.

Disadvantages:

- Particular force field applicable only for a limited class of molecules.
- Does not calculate electronic properties.
- Requires experimental data (or data from ab-initio) for parameters.

Best for:

- Large systems (1000 of atoms)
- Systems processes with no breaking or forming of bond.

iv. Molecular Dynamics

The calculation applies the laws of motion to the molecules. Thus one can stimulate the motion of an enzyme as it changes shape on binding to a substrate or motion of a swarm of water molecules around a molecule of solute. Thus very large molecules approximately one lakh can be studied only with MM and MD.

Thus very large molecules can be studied only with molecular mechanics, because other methods (quantum mechanical methods, based on Schrodinger equation; Semi-empirical, ab-initio and OFT) would take too long. Novel molecules, with unusual structures, are best investigating with ab-initio or possibly DFT calculations. Since the parameterization inherent in MM or SE methods make them unreliable for molecules, which are very different from those used in the parameterization. [Ramachandran, *et.al* , 2008]

1.5) DENSITY FUNCTIONAL THEORY

Density functional theory calculations on the molecules is based on two theorem published by Hohenberg and Kohn in 1964, that is called Kohn-Sham approach. DFT calculations are usually faster than Ab-Intio and it deals with system around 1000 atoms. The only errors are due to approximation in the functional. In DFT, the total energy is expressed in terms of the total one-electron-density rather than the wave function. In this type of calculation, there is an approximate Hamiltonian and an approximate expression for the total electron density. DFT methods can be very accurate for little computational cost. Some methods combine the density functional exchange functional with the Hartree–Fock exchange term and are termed hybrid functional methods .

Density functional theory is ultimately derived from quantum mechanics from 1920's. Especially the Thomas Fermi- Dirac model and the Slater's fundamental work in quantum chemistry. The DFT approach is based upon a strategy of modeling electron correlation via general functional of the electron density. It does not calculate a wave function but rather derive the electron distribution directly. [Arslan , *et.al,* 2007]

This method is good for calculation of geometrics of molecule and transition states, energies, vibration frequencies, dipole moment, charges and bond order and for calculating quantities relevant to thermodynamics and kinetics with accuracy comparable to mp_2 calculation in roughly the same time as needed for HF calculation.

The idea behind DFT is that the energy of a molecule can be determined from the electron density instead of a wave function. It was originated from a theorem by Hohenberg and Kohn which states that the ground state electronic energy is determined completely by the electron density ρ. In other words there exist a one-to-one correspondence between electron density of a system and the energy. It could not provide the exact nature of the functional by which ē density could be converted to energy. Modern DFT method is based on the suggestion by Kohn and Sham in 1965 that the electron kinetic energy should be calculated from an auxiliary set of orbital, Kohn –Sham orbital used for representing the ē density.

DFT includes ē correlation in its theoretical basis. DFT appears to be the method of choice for geometry and energy calculation on transition metal compounds, for which conventional ab-initio calculation often give poor result. It works with electron density which can be measured and is easily grasped rather than a wave function. The main problem associated with

DFT is the inability to systematically improve the result and the known failures to describe certain important features, such as vander wall's interaction.

DFT solved the equation $H\Psi=E\Psi$ in a different way compared with ab-initio methods. Ab-initio method tries to obtain the Eigen wave function $\Psi\ (r_1, r_2 \ldots\ldots rn)$ of the system. The expectation value of a physical property in a particular state described by $\Psi\ (r_1, r_2 \ldots\ldots rn)$ is given by

$$\langle O \rangle = \langle \Psi\ (r_1, r_2 \ldots\ldots rn)\ |O|\ \Psi\ (r_1, r_2 \ldots\ldots rn) \rangle$$

$$= \int \Psi^*(r_1, r_2 \ldots\ldots rn)\ O\ \Psi\ (r_1, r_2 \ldots\ldots rn)\ dr_1, dr_2 \ldots\ldots drn.$$

Generally O is the sum overall one and two particular interaction and thus

$$\langle O \rangle = \int \Psi^*(r_1, r_2 \ldots\ldots rn)\ F\ (1)\ \Psi\ (r_1, r_2 \ldots\ldots rn)\ dr_1, dr_2 \ldots\ldots drn.$$

$$\int \Psi^*(r_1, r_2 \ldots\ldots rn)\ G\ (1, 2)\ \Psi\ (r_1, r_2 \ldots\ldots rn)\ dr_1, dr_2 \ldots\ldots drn.$$

$$\int F\ (1)\ \rho\ (r_1, r_2) + \int G\ (1, 2)\ \rho\ (r_1, r_2, r_1, r_2)\ dr_1, dr$$

Where

$$\rho\ (r_1,r_2) = n \int \Psi^*(r_1,r_2 \ldots\ldots rn)\ F(1)\ \ \Psi(r_1,r_2 \ldots\ldots rn)\ \ dr_2 \ldots\ldots drn$$

$$\rho\ (r_1,r_2, r_1,r_2) = n\ (n\text{-}1) \int \Psi^*(r_1,r_2 \ldots\ldots rn)\ F(1)\ \ \Psi(r_1,r_2 \ldots\ldots rn)\ \ dr_3 \ldots\ldots drn$$

Thus, the expectation value of any physical property can be expressed as a function of the electron density.

1.5.1) Electron Density

The square of the wave function. Total electron density due to N ē Can be defined as N times the integral of square of wave function over the spin coordinates of all ē and overall but one of the spatial variables.

In particular, the total energy can be written as,

$$E = \int Vext\ \rho\ (r)\ dr_1 + \int \Psi^*(T+Vee)\ \Psi dr_1 \ldots\ldots\ldots drn = \int Vext\ \rho\ (r)\ dr_1\ \ +\ \ F\ (\rho)$$

Where,

Vext = External potential

T = the kinetic operator

Vee = Two ē interaction operator

F (ρ) = Function of ρ

Hohenberg and Kohn showed that non-degenerate state density ρ uniquely determined by Vext or vice versa. By applying Hohenberg-Kohn variation principle to the above equation Kohn and Sham derived an exact single – particle self consistent equation similar to HF equation.

$$Fks\ \varphi(r) = \sum\varphi(r)$$

Where

$$Fks = -\tfrac{1}{2}\sum \nabla^2 \ (i) + Veff$$

$$Veff = Vext + \int\rho(r)/\, r_{12}\, dr + Vxc$$

$$P(r) = \sum i\, \nabla^2 \ |\varphi\ i\ (r)\ |^2$$

Vxc= the exchange – correlation potential

The total energy of the system is given by

$$E = Ev + Er\ (\rho(r) + Ej\ (\rho(r))$$

Where

Ev is $\int Vext\ (r)\ dr$

Er is the kinetic energy of Independent electrons

Exc is the exchange correlation energy. Various DFT methods differ from each other in the way deal with Exc (ρ). In generalized gradient approximation (GGA). The total density approximation (LDA) approximates the Exc (ρ) as

$$Exc = \int\sum xc\ [\rho(r)]\ \rho\ (r)\ dr$$

In practice Exc is divided into two parts Exchange Ex and correlation Ec,

$$Exc = Ex + Ec$$

1.5.2) Basis set

A basis set in theoretical and computational chemistry is a set of functions (called basis functions) that is used to represent the electronic wave function in the Hartree-Fock method or density-functional method in order to turn the partial differential equations of the model into algebraic equations suitable for efficient implementation on a computer. It describes the shape of the orbital in an atom. Molecular orbital and entire wave functions are created by taking linear combination of basis function and angular functions. Thus the list of all basis function used in a calculation is called a basis set. . [Krishnan, *etal, 1980]*

It is a set of basis functional building block that can be stacked or added to have the features that we need. By stacking in mathematics, we mean adding things possibly after multiplying each of them by its own constant.

$$\Psi = a_1\Phi_1+a_2\Phi_2+\ldots\ldots ak\ \Phi k \qquad - (1)$$

k = Size of basis set

Φ_1, $\Phi 2 \ldots\ldots \Phi k$ = Basis functions

$a_1 \ldots ak$ = Normalizations constant

John c Slater who first termed to orbital computation using basis sets. The solution for Schrodinger equation for the Hydrogen atom and other one ē ions gives atomic orbitals which are a product of radial function and spherical harmonics or angular function. Strictly speaking atomic orbitals are the real solutions of the Hatree –Fock equations for the atom ie, wave functions for a single ē in the atom. Anything else is not really an atomic orbital function; hence these functions are named as “basis function” . [Jankowski, *et.al,* 1985]

The general expression for a basis function,

$$BF = Ne^{(-\alpha\gamma)} \qquad - (2)$$

N = Normalization constant

α = Orbital exponent

γ = Radius in angstroms

1.5.3) Kinds of Basis function

i. Slater type orbital (STO)

In the early days of quantum chemistry so-called Slater type orbitals(STOs) were used as basis functions due to their similarity with the eigen functions of the hydrogen atom.STO depend on quantum numbers n, l, m (principle quantum number, angular, magnetic quantum numbers) and α (Slater orbital exponent). STO has the general functional form as,

$$\Psi\alpha, n, l, m\ (^{r,\ \theta,\ \Phi}) = N\, r^{n-1}\, e^{-\alpha r}\, Ylm \qquad -(3)$$

Where,

r, θ, Φ = spherical coordinates

Y lm = angular momentum part

α = (z-s/n). s (screening constant)

However the STO's do not have radial nodes. Nodes in the radial part are introduced by making linear combination of atomic orbitals. The linear function can be expressed in exponential form which describes the radial part is called a Slater function.

$$\Phi_{(r)} = e^{(-\alpha r)}$$

Simplifying the above equation for the Hydrogen like system, the STO equation takes the form of,

$$STO = (\alpha^3/\prod)\ ^5 e^{-\alpha r} \qquad - (4)$$

STO's are approximate solution to the Eigen value equation represented by eq (1).

Thus for one electron atoms the wave equation can be written as,

$$\Psi 1s = (\alpha^3/\prod)\ ^5 e^{-\alpha r} \qquad -(5)$$

Advantages of STO

- Physically the exponential depend on distance from the nucleus is very close to the exact hydrogenic orbitals

- Ensure fairly rapid calculation with increasing number of functions
- They provide reasonable representation of atomic orbitals

Disadvantages of STO

- They are not suitable for fast numerical calculations especially 3 and 4 centre integrals cannot be performed analytically.
- In the expression there is no radical nodes .This can be introduced by making linear combination of STO's.

ii. Gaussian Type Orbital (GTO)

In the 1950's Frank boys from Cambridge University in the UK suggested a modification to the wave function by introducing Gaussian type function which contains the exponential $e^{-\beta r2}$ rather than $e^{-\alpha r}$ of the STO's. Such function neither represents the electron density of the real solution nor the STO's. But we can overcome this difficulty to a large extend by using more GTO's. Each basis function in this approach consists of several GTO's combined together in a linear manner with fixed coefficient. Thus we might define a GTO (3G) basis function as,

$$\text{GTO (3G)} = C1\, e^{-\beta_1 r2} + C_2\, e^{-\beta_2 r2} + C_3\, e^{-\beta_3 r2} \qquad - (6)$$

Where the three values of C and β are fixed and that number is included in the designation. These values can be found in several ways, one method is to fit the expression into STO using a least square method.

The GTO has general formula,

$$\text{GTO} = \Psi\alpha, n, l, m^{(r,\, \theta,\, \Phi)} = Ne^{-\beta r2}\, Ylm^{(\theta,\, \Phi)}\, r^{2n-2-l}$$

1.5.4) Types of basis sets

i. STO-3G

This is a minimal basis set, although some atoms have actually more basis functions that are needed to accommodate all the electrons. This basis set introduce us the basic concept of contraction shell in contracting Gaussian from primitive Gaussian. The Gaussian have common exponent. Carbon has one 1s orbital and one sp shell. This means that the 2s and the 2p Gaussian share common d exponent.

ii. 3-21G and 3-21G*

In 3-21G basis set, they split each valence orbital into two parts, an inner shell and an outer shell. The basis function of the inner shell is represented by two Gaussian function , and that are the outer shell by one Gaussian the core orbitals are each represented by one basis function, each composed of three Gaussian.

In 3-21G basis here Lithium to Neon has a 1s function and inner and outer 2s, $2p_x$,$2p_y$, $2p_z$ functions for the total of nine basis function these inhibit three contraction cells a 1s and sp inner and an sp outer contraction shell. For molecules beyond the atom of the first row this simple 3-21G basis set tend to give poor geometries. This problem is largely over come for second row elements by adding a function called polarization function.

iii. 6-31G*

This is a split valence basis set with functions. The valence shell of each atom is split into an inner part composed of 3-Gaussian and an outer part composed of one Gaussian ,while the core orbital are represented by basis function s each composed of 6 Gaussian, the polarization are present on the heavy atom those beyond Helium . Thus Hydrogen and Helium has a 1s orbital represented by the inner 1s' and outer 1s" basis function making two basis function. Carbon has a 1s function represented by 6 Gaussian, an inner 2s,2px,3py,2pz functions each composed of 3 Gaussian. The Gaussian and six 3d function making a total of 1s basis function calculated on 6-31G*basis also called 6-31G [d].

The 6-31G* is probably the most popular set at present, It give good geometry and often relative energies. In general it is much better than 3-21G* basis set for geometry optimization. The 6-31G basis set adds polarization functions only to so called heavy atoms. Sometimes it is helpful to have polarization on Hydrogen as well. It probably offers little advantages over the 6-31G unless the Hydrogen are engaged in some special activity like hydrogen bonding or bridging.

1.5.5) Classification of basis sets

i. Minimal basis set

In a minimal basis set we select one basis function for every atomic orbital's that is required to describe the free atom that is, minimal basis sets contain the minimum number of basic functions need for each atoms. Minimal basis sets are five atomic type orbitals. In minimal basis sets each atomic orbitals represented by one STO which is fit with n- GTO. Here minimum numbers of atomic orbitals are used. We take all the orbitals requiring for the filling up of electrons. There for this is also known as a single zeta basis set (sz). The STO-KG or STO-Ng basis set is a minimal basis set which takes the linear combination of KGTOs to STO. The commonly used STO-KG minimal basis set is STO-3G. Since a minimal set incorporates only a single set of valence functions for each symmetry type. It is not capable of describing non-spherical electron distribution in molecules .

The individual GTO's are called primitive orbitals. While the combined functions are called contracted functions. Thus when a basis function contains more than one primitive Gaussian it can be considered as contracted. The STO-3G series basis set is a minimal set where each basis function is a contraction of 3 primitive Gaussians. Therefore the STO-3G basis set for methyl thus consist of a total number of a contracted functions built from 27 primitive functions.

ii. Correlation – consistent basis set

All the previously designated basis sets are POPLE (from the group of John Pople) basis sets. Another class of popular basis sets was developed by the research group of dunning. These are specially designed for post Hatree-Fock calculations, in which electron correlation is better taken in to account than at the Hatree-Fock level. They are intended, ideally, to give with such calculations improved results in step with nine correlated with their increasing size, and so they are called correlation consistent basis sets.

The correlation consistent basis sets are designated ccpVTZ

P — Polarization function

X —Number of shells the valence function is split

V —Valence

Z —Zeta

I.e., ccpVTZ — Correlation Consistent Polarized Valence Doubly Split Zeta

CcpVTZ — Correlation Consistent Polarized Valence Triply Split Zeta

These basis sets can be argument with diffuse and extra polarization function, giving Augmented – cc- Pvxz sets.

iii. Polarized basis sets

Split valence basis set allow orbital to change size, but not to change shape. Thus limitation can be removed by orbitals with angular momentum beyond what is required describing ground state of each atom. The quantitative importance of polarization function is that they permit the molecular function more flexibly to distort away from spherical symmetry in the neighborhood of each atom. The distortion of s, p and α orbitals can be made by the inclusion of p, d and f functions respectively in the basis set. This leads to double – zeta polarization or split valence plus polarization basis set. The commonly used 6-31G (d) basis set is formed by adding d- type functional to non – hydrogen atoms to the 6-31G basis set . In the cases where the description of the hydrogen atom is important, set of p – type orbitals are usually added, for the example the 6-31G (d,p) is the 6-31G (d) basis set is formed by adding a set of p type orbitals to hydrogen atoms. In a similar manner, the 6-31G (d) and 6-31G (d, p) basis sets are formed from the 6-31G basis set.

iv. Split valence basis set

The simplest way to improve the flexibility of a basis set is to increase number of basic functions on each atom. A basis set formed by doubling the functions of a minimal basis set is usually termed a double – zeta basis set. If only the valence functions of a minimal basis set is doubled, the basis set is ruffed to as split valence basis set. The commonly used split valence basis sets are 3-21G and 6-31G basis set. In the 3-21G basis set, each inner orbital of an atom is formed by taking a linear combination of two and one GTO's respectively. The triple zeta basis set 6-31G is formed by further splitting the valence orbital into three sets of orbitals. This was proposed by John Pople and his group in the late 1970's They are an expansion of basis sets make the total are not in the valence shell and two functions for those in the valence shell.

v. Plane polarized basis sets

Split valence basis sets allow orbital to change size. But not to change in the shape. This limitation can be removed by adding orbitals with angular momentum beyond what is require describing ground state of each atom. The qualitative importance of polarization functions is that they permit the molecular wave function more flexibly to distort away from spherical symmetry in the neighborhood of each atom. The distortion of s, p and d orbitals can be made by the inclusion of p, d and f functions respectively the basis set. This leads to double- zeta plus polarization (DZP) or split valence plus polarization (SVP) basis set. The commonly used 6-31G (d) basis set is formed by adding d- type functional to non hydrogen atoms to the 6-31G basis set. In the cases where the description of the hydrogen atom is important, a set of p- type orbital is usually added.

Example: The 6-31G (d) basis set formed by adding a set of p type orbital hydrogen atom. In a similar manner, the 6-311G(d) and 6-311G(d, p) basis sets are formed from the 6-311G basis set.

vi. Multi Zeta Valence Basis Set

To overcome the deficiency of minimal basis set others basis set has been developed.

vii. Double Zeta basis set:

These have twice the number of function for each orbital. Thus hydrogen atom would have two functions, carbon and oxygen has ten functions each.

viii. Triple Zeta basis set:

Have thrice the number of functions compared to minimal basis set.

1.6) HARTREE-FOCK METHOD

In computational chemistry the HF method is an approximation for the determination of the wave function and the energy of a quantum many body system is a stationary state. In Huckel theory the molecular orbitals and molecular orbital energies are derived using one- electron formalism. And it is assumed that the energy of a many electron system could be determined simply as the sum of the energies of the occupied one electron orbitals.

The ubiquity of orbital concepts in chemistry is a testimony to the predictive power and intuitive appeal of HF-Mo theory. However, it is important to remember that these orbitals are mathematical constructs which only approximate reality. As long as we are content to consider molecules near their equilibrium geometry, HF theory often provides a good starting point for more elaborate theoretical methods which are better approximations to the electronic Schrodinger equation.

The HF equation can be solved numerically (exact HF) or they can be solved in the space spanned by a set of basis functions [HF Roothan equation]. In either case the solution depend on the orbitals. Hence we need to guess some initial orbitals and then refine our guesses interactively. For this reason HF is called self consistent field (SCF) approach.

Restricted and un restricted HF method

Although no strictly part of a model chemistry, there is a third component to even Gaussian involving how electron spin is handled, whether it is performed using an open shell model or a closed shell model. The two options are referred to a restricted and un restricted calculations. For closed shell model molecule having an even number of electron divided into pairs of opposite spins a spin restricted model is a default. In other words closed shell calculations use doubly occupied orbitals, each containing two electrons of opposite spins.

1.7) INFRARED SPECTROSCOPY

If we consider a diatomic molecule with masses m_1 and m_2 respectively execute simple harmonic oscillation, then its stretching frequency is given by

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

where k is the force constant and $\mu = \frac{m_1 m_2}{m_1+m_2}$.

In reality the vibration may not be of simple harmonic nature, so the vibrational wavenumber is obtained as $\bar{\upsilon}_0 = \bar{\upsilon}_e\left[1-\left(\upsilon+\frac{1}{2}\right)x_e\right]$

where x_e is the anharmonicity constant, υ is the vibrational quantum number and $\bar{\upsilon}_e$ oscillation frequency of the anharmonic system.

The atoms in a molecule usually execute different types of vibrational motion. They excite to a higher vibrational level if radiation of same frequency that of its quantized vibration is allowed to fall on them. The molecules absorbing a quantum of energy give rise to bands from about 200 cm^{-1} to 4000 cm^{-1}. Functional groups have characteristic vibrational frequencies and these groups can be identified by their characteristic vibrational frequencies. This makes vibrational spectra one of the most reliable methods for the understanding of the structure of the molecules. IR region of the electromagnetic spectrum is considered to cover the range from 50 to 12500 cm^{-1}. It is generally subdivided into three regions- near IR (12500-4000 cm^{-1}), middle IR (4000-400 cm^{-1}) and the far IR (400-50 cm^{-1}). The middle IR is the region most commonly employed for standard laboratory investigations as it covers most of the vibrational transitions.

1.7.1) Infrared selection rules

A molecule can absorb a photon of energy $h\upsilon$ and make a transition from the state φ_i to φ_j if the energy difference between the two states is equal to the photon energy. The probability of transition from a state i to j is proportional to the square of the transition moment given as

$$\mu_{ij} = \int \varphi_i^* \mu \varphi_j d\tau$$

where, μ is the operator for the dipole moment of the molecule. The dipole moment of a molecule is a function of the normal coordinate Q_k of the vibrational mode and can be expanded using the Taylor series

$$\mu = \mu_0 + \left(\frac{\partial \mu}{\partial Q_k}\right) Q_k + \cdots$$

Neglecting the higher order terms and substituting this in the expression for μ_{ij},

$$\mu_{ij} = \int \varphi_i^* \mu_0 \varphi_j d\tau + \int \varphi_i^* \left(\frac{\partial \mu}{\partial Q_k}\right) Q_k \varphi_j d\tau$$

$$\mu_{ij} = \mu_0 \int \varphi_i^* \varphi_j d\tau + \left(\frac{\partial \mu}{\partial Q_k}\right) \int \varphi_i^* Q_k \varphi_j d\tau$$

The first term will vanish and the second term is non zero if $\left(\frac{\partial \mu}{\partial Q_k}\right)$ is finite at least for one component of dipole moment. That is, for a mode of vibration to be IR active, the vibrational motion of that mode must give rise to a change in dipole moment. Also the integral $\int \varphi_i^* Q_k \varphi_j d\tau$ must be finite which is possible only if the vibrational quantum number change as $\Delta\nu = \pm 1$ for harmonic approximation. For anharmonic approximations $\Delta\nu = \pm 2, \pm 3, \ldots$. The symmetry of the molecule also restricts activity of vibrations. Homonuclear diatomics have no dipole moment and also no change in dipole moment during vibration. So vibrational spectra are observable only in the case of heteronuclear di atomics [Aruldas , *et.al*, 2004].

1.7.2) FT-IR Spectroscopy - Instrumentation and theory

Fourier Transform is a simple mathematical technique to resolve a complex wave into its frequency components. It is employed in infrared spectroscopy (i.e. FT-IR) for the detection of very weak signals, and is useful even in the far IR regions where the conventional spectrometers fails as the sources are weak and detectors insensitive. The absorption spectrum in a Fourier transform infrared spectrometer is obtained through interference technique, like almost all diffraction methods. The structural information from the observed diffraction patterns are obtained by Fourier transformation, accomplished using digital computers.

The principle of interferometry is the simple interference of radiations. Fourier transform infrared (FT-IR) spectroscopy too is an interference technique through which recent advances in digital computer technology has demonstrated in superiority to dispersive IR techniques. Fourier transform spectroscopy uses the Michelson interferometer as the multiplex optical device [Griffiths and De Haseth 1986].

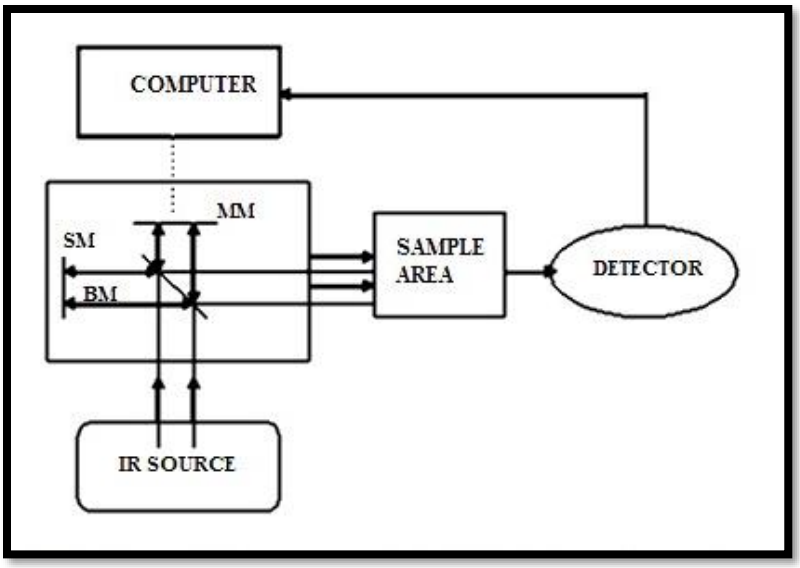


Fig 1.7.1

Block diagram of FT-IR Spectrometer

i. **Source**

The most commonly used radiation source is globar operating on the basis of the block body radiation. It consists of a SiC (silicon carbide) dimensions 2 cm in length and 0.5 cm in diameter heated to about 1450 K. The globa is generally used in the spectral range up to 100μm. The globar is operated in vacuum only. Nernst glower (sintered mixtures of the oxides of Zr, Tm, Ce, Y, and Er) is also used as source in some spectrometers depending upon the spectral range. For more sophisticated applications, gas plasma must be used as radiation source. Besides thermic Microwave generators like klystrons or magnetrons are also used for wide frequency range.

ii. Detector

There are two detector commonly used depending upon the energy reaching the detector. A normal detector for routine work function is based on pyroelectric effect. Crystals such as deuterium triglycine sulphate in temperature resistant alkali halide window, with a permanent electric dipole moment respond to a sudden change in the dipolar order with the generation of compensating surface charges. IR or heat pulses can be origin if such induced disorder. The voltage accompanying the compensation charges can be used to detect the IR to the heat pulse.

The commonly used system is the Golay detector which works under a pneumatic principle. A thin film absorbs the incident IR light. The generated heat increases the pressure in the gas chamber which drives a mirror. The mirror is a part of an optical system that images a grating onto itself. Any small motion of the mirror leads to change in the overlap between grating and the image and thus gives a signal to the detector.

iii. Interferometer

The interferometer is the heart of the FT-IR instrument. The interferometer is the bit that analyses the IR or near IR and hence enable us to generate the spectrum. The classic Michelson interferometer is shown in Fig.1.7.2 contains a source, detector, stationary and moving mirrors and a beam splitter; here LS - Light Source, L1, L2 - Lenses, M1, M2 - Mirrors, D - Detector, BS - Beam Splitter.

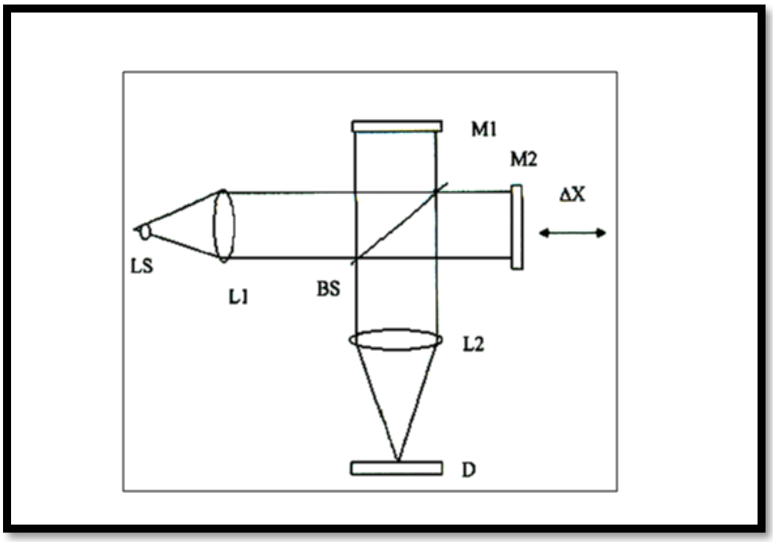


Fig.1.7.2

Michelson Interferometer – Optical path

The beam splitter is the crystal of potassium bromide coated with germanium [Mile *et al*., 1985], splits the incident light equally reflecting half to the stationary mirror while transmitting the other half to the moving mirror. The white light from the source located at the focus of lens L_1 is separated into two parts by the beam splitter. The reflected part is focused into the detector D after reflection from the stationary mirror M_1 and after a second split by the beam splitter. The transmitted part of the light is also focused onto the detector after it was reflected from the moving mirror M_2 is movable, which produce the path difference between the two beams thereby develop interference pattern at the detector. Their intensity $I(x)$ depends on the position x of the mirror M_2. $I(x)$ is termed interferogram function.

If the incident beam is monochromatic of the form $E(x,t) = E_0 cos(kx - \omega t)$, the field E_0 at the detector is

$$E_D = \frac{1}{2}\{E_0 cos(\overline{\omega_0}t - k_0 x) + E_0 cos[k_0(x + 2\Delta x) - \overline{\omega_0}t]\}$$

where, $2\Delta x$ is the optical path difference between the two beams. The intensity at the detector is given by the following expression

$$I(x) = c_0\varepsilon_0\langle E^2\rangle = \frac{c_0\varepsilon_0}{4}E_0^2[1 + cos(4\pi\upsilon_0 x)]$$

In terms of spectral intensity, $I(\upsilon) = c_0\varepsilon_0 E_0^2\delta(\upsilon - \upsilon_0)/2$, the above equation can be written as

$$I(x) = \frac{1}{2}\int_0^\infty I(\upsilon)\,[1 + cos(4\pi\upsilon x)]d\upsilon$$

Generalizing this equation to an arbitrary intensity spectrum $I(\upsilon)$ yields the basic relationship for Fourier spectroscopy.

$$I'(x) = I(x) - \frac{1}{2}\int_0^\infty I(\upsilon)d\upsilon = \frac{1}{2}\int_0^\infty I(\upsilon)cos(4\pi\upsilon x)d\upsilon$$

The interferogram function $I(x)$ or $I'(x)$ contains the whole information about the spectrum $I(\upsilon)$. In fact, $I'(x)$ is the Fourier transform of $I(\upsilon)$performed with the cosine function. The observed intensity $I(x)$oscillates around an average intensity $I_0/2$ which is exactly half of the original total intensity of the beam.

For $x = 0$, it reaches its maximum value of I_0. This position corresponds to zero optical path differences. It is called white light position. For $x = \infty$, the coherence of the radiation is lost, and therefore the intensity at the detector becomes $I_0/2$.

A Fourier transformation of $I'(x)$ yields for $x = y/2$,

$$\int I'\left(\frac{y}{2}\right)\cos(2\pi\upsilon' y)\, dy = \frac{1}{2}I(\upsilon)d\upsilon \int cos(2\pi\upsilon y)cos(2\pi\upsilon' y)\, d = I(\upsilon')/2$$

Since the integration over y gives $\delta(\nu - \nu')$. This equation shows that the spectral components of the light are obtained directly from the inteferogram by Fourier transformation, without any spectral dispersion [Kuzmnay 1998]. This Fourier spectroscopy has many basic advantages when compared to dispersive spectroscopy.

The ‘energy advantage’ originates from the fact that during the whole period of measurement nearly always the total beam intensity is captured by the detector. This means the detection operates on a high signal level which improves the signal-to-noise ratio, particularly for weak radiation sources.

The ‘Fellgett’ or the ‘multiplex advantage’ originate from the simultaneous measurement of full spectrum. To obtain spectra from radiation of very low intensity such as from astronomical sources, all the frequencies are recorded simultaneously during spectroscopy as in dispersive spectroscopy, they are said to be ‘multiplexed’. In dispersive spectroscopy N parts of the widths $\Delta\nu$ of the spectrum will be measured successively so that for each part only the time T' =T/N is available. The signal-to-noise ratio would be smaller by $\frac{1}{\sqrt{4N}}$.

Interferometer also has greater ‘throughput’ than dispersive IR methods. ‘Throughput’, a measure of the optical efficiency of the system, is defined as the product of the area and solid angle of the beam passing from the source to the detector. Since there is no slit in FT-IR spectrometer, the cross section of the beam of radiation in an interferometer can be much larger than that of a dispersive spectrometer, which leads to considerable improvements in signal-to-noise ratio. But in much chemical and analytical application the sample size limits the energy advantage. The optimum resolution is obtained by using the theoretical relationship, $r = F\sqrt{\frac{2}{R_0}}$. Here r is the radius of the entrance pinhole and R_0 is the resolution. This yields for the brightness of the interferometer.

$$E = (r^2 \pi A^2) / F^2 = (2\pi A^2) / R_0 = (2\pi A^2) / \nu)\, \delta \nu$$

where A is the beam diameter in the spectrometer. For dispersive spectrometer the brightness is given by

$$E = (AR_0 H \delta\lambda) / F$$

where, H and F are the height of the slit and the focal length of the grating spectrometer respectively. By comparing these two equation it is found that for Fourier spectrometer the enhancement of the brightness is of the order of 500 times greater than the grating and prism spectrometer known as the ‘Jacquinot advantage’.

The dispersive spectrometer suffer from greater wavenumber errors, of a less predictable form owing to their general mechanical and thermal instability and can also be affected by non-uniform illumination across the monochromator entrance slit . FT spectrometer typically uses the He-Ne lasers as a reference beam to monitor the displacement of the moving optical element, so providing an active internal absolute wavelength calibration [Cones and Cones 1966]. This feature of FT spectrometers is known as the ‘Cannes advantage’.

1.8) UV-VISIBLE SPECTROSCOPY

UV-Visible/NIR spectroscopy(UV-Vis Spectroscopy) can be divided into ultraviolet, visible, and near-infrared regions of the spectrum, depending on the wavelengths used. since its frequency is close to the overtone frequency of many natural vibrations, weak substance-specific absorption bands can be detected. It can therefore be used for non-destructive measurements, such as determining the sugar, lipid, protein content of foodstuffs and for identifying medicinals.

1.8.1) Principle of UV-VIS Spectroscopy

UV-visible spectroscopy exploits the wave-like nature of electrons and its interactions with electromagnetic radiation. UV-Vis spectroscopic instruments are used to identify, characterize, and quantify an extraordinary wide range of molecular compounds. It can be used for non-destructive measurements, such as determining the sugar, lipid, protein content of foodstuffs and for identifying medicinals.

When a material is irradiated with an electromagnetic wave, phenomena such as transmission, absorption, reflection, and scattering can occur. Absorption occurs when the energy of incoming light is equal to the energy difference (ΔE) between a molecule's ground and excited states. The excitation of an electron from the ground state to an excited state is described as an electronic transition (Figure 1.8.1).

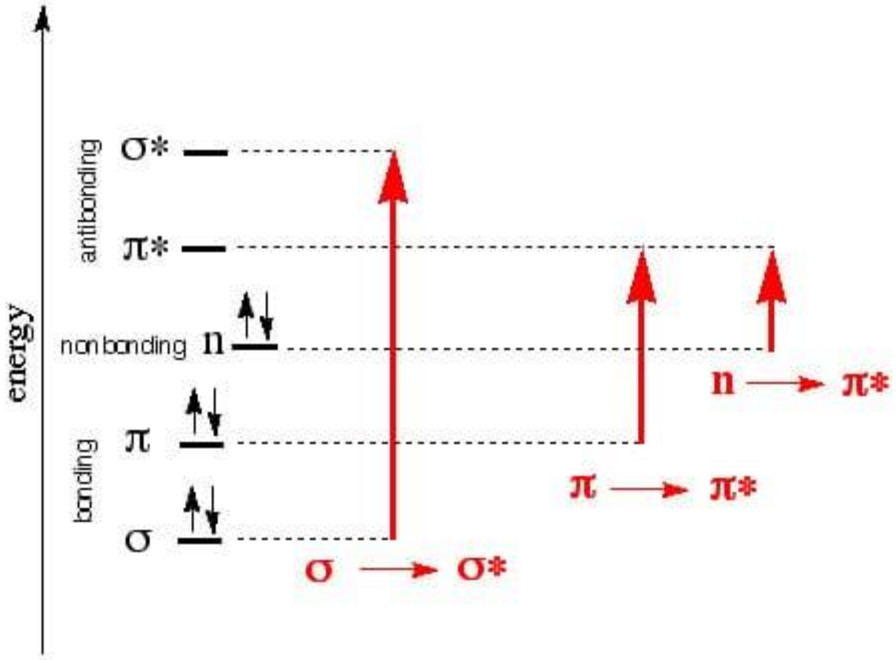


Fig 1.8.1

Excitation of an electron from the ground state (S0) to the excited state (S1).

The relationship between the energy difference and wavelength is described by the Plank equation.

$E=h\nu=hc/\lambda$

where *E* is the energy required to promote an electron from the ground to excited state, *h* is Planck's constant, ν is the wavenumber, *c* is the speed of light, and λ is the wavelength.

Planck's equation demonstrates that the less energy needed to excite the electrons, the longer the wavelength of the absorption band. The absorption bands are indicative of the molecular structure of the sample and will shift in wavelength and intensity depending on the molecular interaction and environmental conditions. These bands are typically broad and featureless due to the numerous molecular vibrational levels associated with the electronic energy levels.

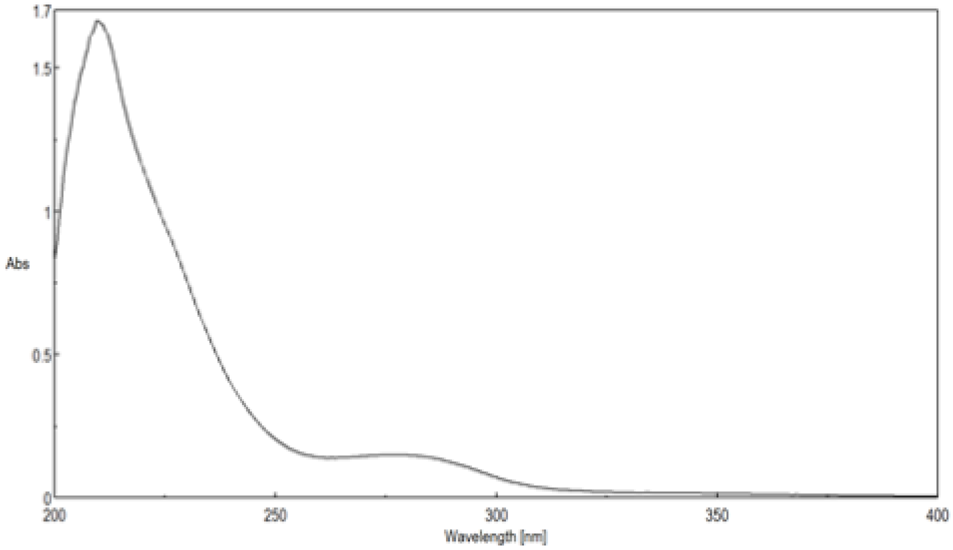


Fig 1.8.2

Example absorption spectrum. The peak around 280 nm requires less energy to promote electrons into the excited state than the peak around 215 nm.

UV-Visible/NIR spectroscopy can be divided into ultraviolet, visible, and near-infrared regions of the spectrum. The ultraviolet region is defined as 180 to 400 nm, visible between 400 and 800 nm, and the near-infrared is from 800 to 3200 nm. Near-infrared light is generally poorly absorbed because its photon energy is insufficient to induce electronic transitions and its frequency is greater than the natural vibration frequency of most chemical bonds. However, since the frequency in the NIR is close to the overtone frequency of many natural vibrations, weak substance-specific absorption bands can be detected.

1.8.2) Beer-Lambert Law

A UV-Visible/NIR spectrophotometer measures the transmittance or the amount of light transmitted through a sample by ratioing the intensity of the incident light (I_0) to the intensity of the transmitted light (I).

$T = I/I_0$

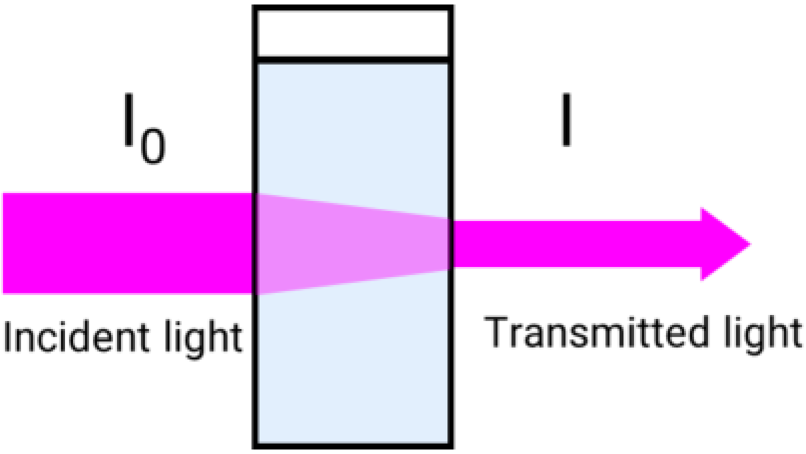


Figure1.8.3

Incident light (I0) passing through a sample that transmit light, I.

The relationship between transmittance and absorbance is described by the following equation

$abs = 2\text{-}\log I/I_0 \cdot 100 = 2\text{-}\log(\%T)$

Absorbance measurements are frequently used to quantify an unknown sample's concentration by exploiting the Beer-Lambert Law that describes how light is attenuated based on the materials it passes through. The transmittance, and therefore the absorbance, are directly proportional to a sample's concentration, c, molar absorptivity, ε , and cuvette pathlength, l.

$A = \varepsilon cl$

The amount of light absorbed by the sample depends on the number of molecules interacted with. The more concentrated a sample is, the more molecules are present and the higher the absorbance. Likewise, the longer the pathlength of the cell, the greater the distance that the light travels through the sample, increasing the number of molecules interacted with and therefore the absorbance. To compare the absorbances of two solutions with either different concentrations or pathlengths, there needs to be a constant variable to normalize the data on. Additionally, to determine a sample's concentration by measuring absorbance, the cell pathlength and the strength of the electronic transition of the chromophore must be known. This constant or the probability of the electronic transition occurring is the molar absorptivity. Since molecules have different electronic transitions of varying strengths, the molar absorptivity will vary depending on the transition being probed and is therefore wavelength dependent.

1.9) ELECTROSTATIC POTENTIAL OF MOLECULES

For a molecular charge distribution, which is essentially a collection of positive discrete nuclear charges Z_A and a continuous negative electron density distribution described by $\rho(\boldsymbol{r})$, the molecular electrostatic potential generated is given in atomic units as

$$V(\boldsymbol{r}) = \sum_A \frac{Z_A}{|\boldsymbol{r}-\boldsymbol{r}_A|} - \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3\boldsymbol{r}'$$

The first term is the bare-nuclear potential, which is always non-negative,the second term is the negative potential, engendered by the continuous electron charge density. The resultant total MEP thus generated can attain positive as well as negative values through zero.

The molecular electrostatic potential can be evaluated using the density matrix **P** and the atomic orbitals $\{\varphi_\mu\}$, as

$$V = \left(\boldsymbol{r} \sum_{A=1}^{N} \frac{Z_A}{|\boldsymbol{r}-R_A|}\right) - \sum_{\mu,\vartheta} P_{\mu\vartheta} \int \frac{\varphi_\mu(\boldsymbol{r}')\varphi_\vartheta^*(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3\boldsymbol{r}'$$

Here φ_μ's are atomic orbitals and $P_{\mu\vartheta}$'s are the corresponding density matrixelements. The ab initio MEP calculations for large molecules are often slow due to the large number of atoms involved, the extensive basis sets employed, as well as the number of grid points over which the MEP is to be evaluated. However several ingenious techniques have been developed for faster computation of MESP. Different mathematical inequalities and numerical checks have been found to be useful for achieving an efficient computation of the MEP. From the above equation it is seen that if a density matrix element $P_{\mu\vartheta}$ is numerically close to zero, then the integrals involving the interaction of φ_μ and φ_ϑ need not be evaluated for any point on the grid. Thus for large molecules, even though N(N+1) integrals are involved, most of them can be neglected depending upon the value $P_{\mu\vartheta}$ and the distance between the centres of the corresponding atomic orbitals. Within a density functional scheme, the Kohn-Sham orbitals could be used in order to compute MEP. The MEP obtained within the framework of the density functional theory (DFT) is also generally found to be in good qualitative agreement with the corresponding HF-SCF one. The suitability of DFT method towards the calculation of electrostatic properties of molecules [Solvia *et al.*, 1997] has been assessed by Solvia *et al.*, It was observed [Solvia *et al.*, 1997] that DFT methods do not noticeably improve the MEP representation at the HF level. However, a more remarkable improvement was seen on employing hybrid non-local functionals. Since DFT is a computationally economical method, it can be gainfully employed for examining molecular electrostatics of larger systems. Since

1990, the DFT based methods have gained popularity for tackling large molecular systems. [Gadre and Shirsat 2000].

1.10) FRONTIER MOLECULAR ORBITALS

The concept of linear combination can be applied to polyatomic molecules and the resulting MOs are delocalized over the entire molecule. These linear combination lead to bonding, anti-bonding or non-bonding MOs. The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are known as frontier molecular orbitals. The ionization energy (I) for an orbital is defined as the energy needed to remove an electron from the orbital to infinite separation, while the electron affinity (A) of an orbital is the energy released when the orbital accepts an electron from infinity [Fukui, 1982]. The orbital energy of the highest occupied MO (HOMO) is approximately equal to the ionization energy and the orbital energy of the lowest unoccupied MO (LUMO) is approximately equal to the electron affinity.

1.11) NONLINEAR OPTICAL PROPERTIES

Conjugated molecules could posses' large nonlinear response. A molecule is said to be conjugated if it contains alternating single and double bonds. A single bond always has the structure of σ bond, while a double bond consist a σ and a π bond. A π bond is made up of the orbital overlap of two p orbitals, one from each atom connected by the bond. The optical response of a σ bond is very different from that of π, because σ electrons tend to be localized in space. In contrast, π electrons tend to be delocalized and hence tend to be less tightly bound and will respond freely to an applied optical field and this tends to produce large linear and nonlinear optical responses. The π electrons tend to be delocalized in the sense that a given electron can be found anywhere along the chain.

Early models of the optical and nonlinear optical properties of delocalized π-electron systems include the "particle in a box" [Kuzyk 2013]. We can model the π electrons of a conjugated chain as being free to move in a one dimensional square well potential whose length L is that of the chain. The polarizabilities are proportional to the higher powers of L . As interest focused on lowest order nonlinear optics and second-harmonic generation, the requirement for a lack of inversion symmetry at the molecular level required molecules with a dipole moment, so that electron donor and electron acceptor terminated π-electron structures became the model. Clearer connections to the quantum mechanical descriptions of these structures emerged through connection to charge transfer within the π-conjugated system and the excited state dipole moment.

Organic molecules posses large optical nonlinearities and hence they invite much interests to be used as nonlinear optical devices. For a molecule to show large hyperpolarizabilities, the electrons required to be highly polarizable so that it would respond quickly to an electric filed. This is achieved through conjugation, where the π electrons are delocalized and could be moved by an electric field. The electron donor and acceptor groups attached at opposite ends of the molecule provide asymmetry to the molecule. A primary requirement for a molecule to have a nonlinear response is that it should possess non centro symmetry. If the conjugation length or the strength between these groups is increased, it will result in large hyperpolarizabilities.

CHAPTER 2

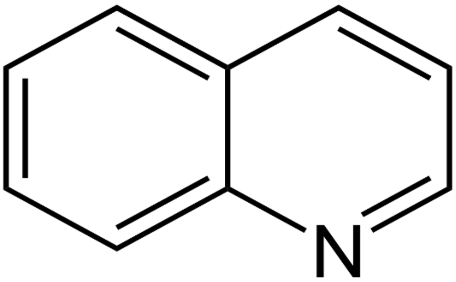
LITERATURE REVIEW

Quinoline is a heterocyclic aromatic organic compound with the chemical formula C9H7N. It is a colorless hygroscopic liquid with a strong odor. Aged samples, especially if exposed to light, become yellow and later brown. Quinoline is only slightly soluble in cold water but dissolves readily in hot water and most organic solvents. Quinoline itself has few applications, but many of its derivatives are useful in diverse applications. A prominent example is quinine, an alkaloid found in plants. Over 200 biologically active quinoline and quinazoline alkaloids are identified. 4-Hydroxy-2-alkylquinolines (HAQs) are involved in antibiotic resistance.[Brown , et.al, 1955).

Quinoline was first extracted from coal tar in 1834 by German chemist Friedlieb Ferdinand Runge; he called quinoline leukol ("white oil" in Greek). Coal tar remains the principal source Std enthalpy of formation (ΔfH ⦵ 298) 174.9 kJ·mol −1 Hazards GHS labelling: Pictograms Signal word Danger Hazard statements H302, H312, H315, H319, H341, H350, H411 Precautionary statements P201, P202, P264, P270, P273, P280, P281, P301+P312, P302+P352, P305+P351+P338, P308+P313, P312, P321, P322, P330, P332+P313, P337+P313, P362, P363, P391, P405, P501 NFPA 704 (fire diamond) Flash point 101 °C (214 °F; 374 K) Autoignition temperature 400 °C (752 °F; 673 K) Lethal dose or concentration (LD, LC): LD50 (median dose) 331 mg/kg Except where otherwise noted, data are given for materials in their standard state (at 25 °C [77 °F], 100 kPa). In 1842, French chemist Charles Gerhardt obtained a compound by dry distilling quinine, strychnine, or cinchonine with potassium hydroxide; he called the compound Chinoilin or Chinolein. Runge's and Gephardt's compounds seemed to be distinct isomers because they reacted differently. However, the German chemist August Hoffmann eventually recognized that the differences in behaviors was due to the presence of contaminants and that the two compounds were actually identical. The only report of quinoline as a natural product is from the Peruvian stick insect Oreophoetes peruana. They have a pair of thoracic glands from which they discharge a malodorous fluid containing quinoline when disturbed. “Defensive Production of quinoline by a phasmid insect (Oreophoetes peruana) Like other nitrogen heterocyclic compounds, such as pyridine derivatives, quinoline is often reported as an environmental contaminant associated with facilities processing oil shale or coal, and has also been found at legacy wood treatment sites.

Owing to its relatively high solubility in water quinoline has significant potential for mobility in the environment, which may promote water contamination. Quinoline is readily degradable by certain microorganisms, such as Rhodococcus species Strain Q1, which was isolated from soil and paper mill sludge. Quinolines are present in small amounts in crude oil within the virgin diesel fraction. It can be removed by the process called hydro denitrification.

STRUCTURE:



USES OF QUINOLINE

(1) Quinoline is used in the manufacture of dyes, the preparation of hydroxyquinoline sulfate and niacin. It is also used as a solvent for resins and terpenes.

(2) Quinoline is mainly used as in the production of other specialty chemicals. Approximately 4 tonnes are produced annually according to a report published in 2005. Its principal use is as a precursor to 8-hydroxyquinoline, which is a versatile chelating agent and precursor to pesticides. Its 2- and 4-methyl derivatives are precursors to cyanine dyes. Oxidation of quinoline affords quinolinic acid (pyridine-2,3-dicarboxylic acid), a precursor to the herbicide sold under the name "Assert".

(3) The reduction of quinoline with sodium borohydride in the presence of acetic acid is known to produce Kairoline A.

(4) (C.f. Kairine) Quinoline has several anti-malarial derivatives, including quinine, chloroquine, amodiaquine, and primaquine.

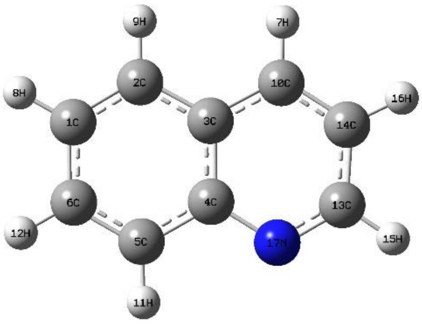
(5) Quinolines are reduced to tetrahydroquinolines enantioselectively using several catalyst systems.

Quinolinium compounds (e.g. salts) can also be used as corrosion inhibitors and intensifiers.

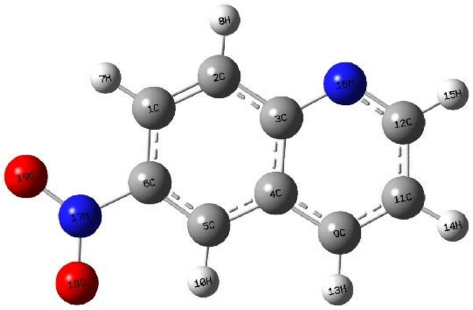
CHAPTER 3

RESULT AND DISCUSSION

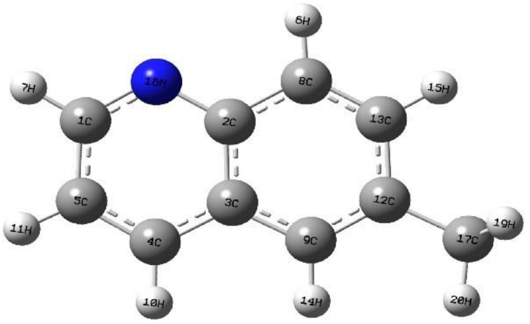
OPTIMIZED STRUCTURE OF COMPOUNDS



QUINOLINE



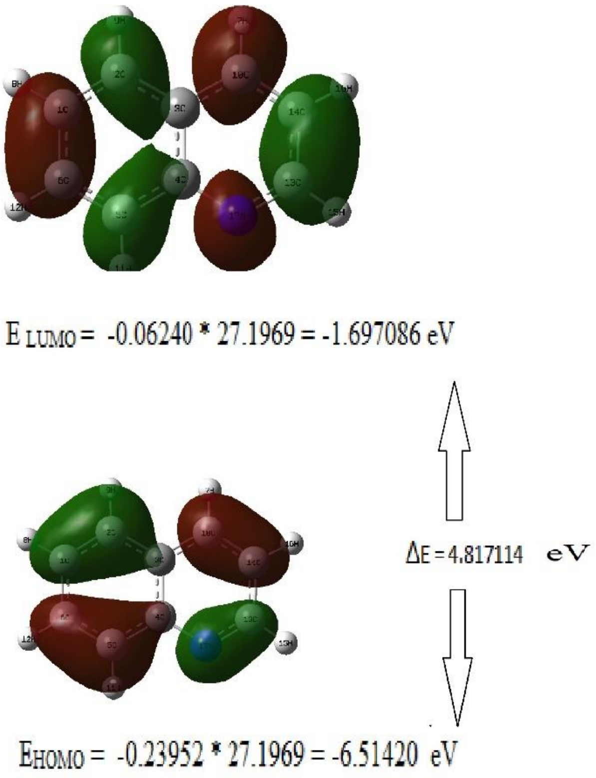
6-NITRO QUINOLINE



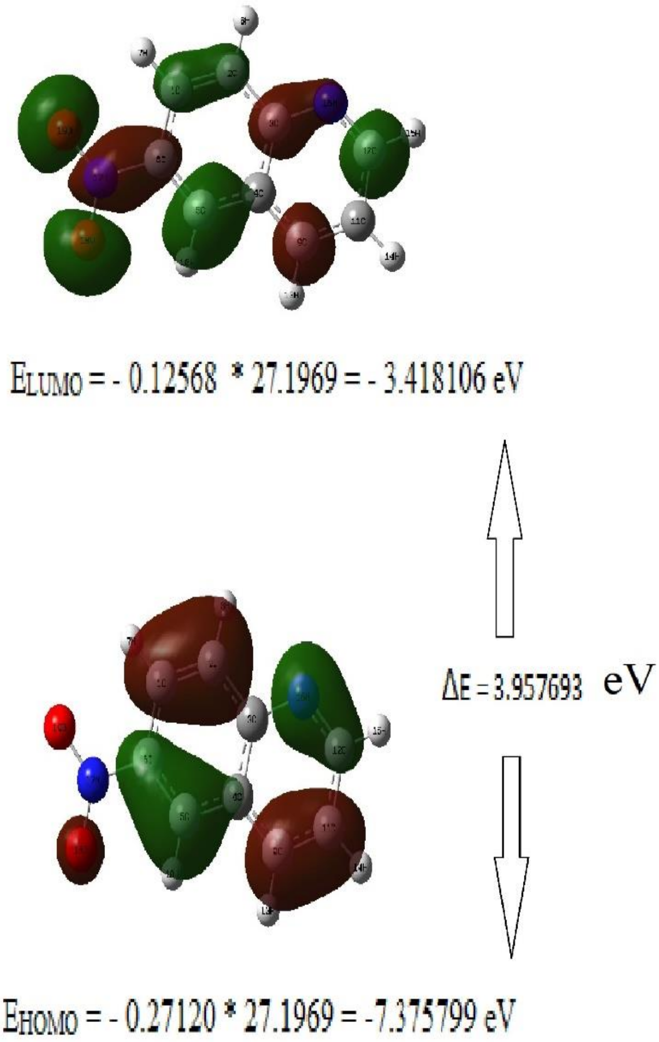
6-METHYL QUINOLINE

FRONTIER MOLECULAR ORBITALS

The frontier molecular orbital (FMO) energies of the compounds were calculated by using the DFT/B3LYP/SDD level. The occupied and unoccupied MOs which are active in electronic transitions for compounds are shown in the figures. It is well known that HOMO energy characterizes the electron giving ability, while LUMO energy characterizes the electron withdrawing ability. Energy gap between HOMO and LUMO exhibits the molecular chemical stability and it plays a critical role in determining molecular electrical transport properties. Obviously, it indicates electron conductivity measurement. It is observed that the values of energy gap for the compounds were found to be 4.817eV for Quinoline , 3.9577eV for 6-Nitro quinoline and 4.8010 eV for 6-Methyl quinoline. The small energy gap between HOMO and LUMO indicates that charge transfer occurs within compounds and can be easily polarized. The lowest energy gap observed At 3.9577 eV for 6-Nitro quinoline compound while the largest value was theoretically found to be 4.817 eV for the Quinoline compound . It is obvious that the substitution of donor group to the Quinoline does not change the Energy gap much but the substitution of a strong acceptor group has lessened the Energy gap.



QUINOLINE LUMO AND HOMO

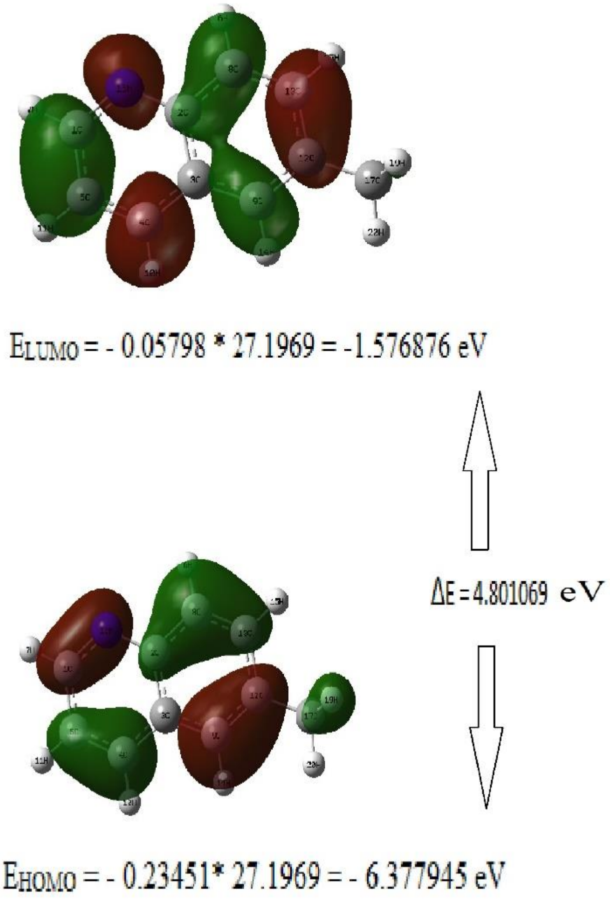


E_{LUMO} = - 0.12568 * 27.1969 = - 3.418106 eV

ΔE = 3.957693 eV

E_{HOMO} = - 0.27120 * 27.1969 = -7.375799 eV

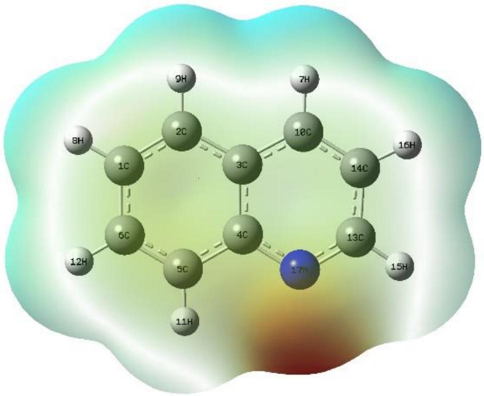
6-NITRO QUINOLINE LUMO AND HOMO

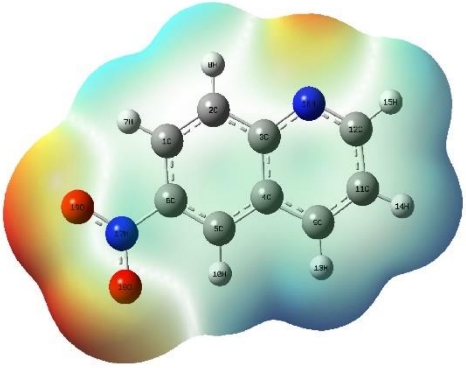


6-METHYL QUINOLINE HOMO AND LUMO

MOLECULAR ELECTROSTATIC POTENTIAL

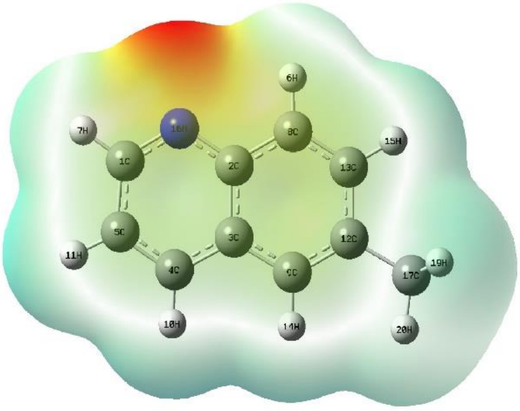
MEP is related to the electron density and is a very useful descriptor in understanding sites for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions [Scrocco and Tomasi 1978; Luque *et al.*, 2000]. The electrostatic potential V(r) is also well suited for analyzing processes based on the "recognition" of one molecule by another, as in drug-receptor, and enzyme-substrate interactions, because it is through their potentials that the two species first "see" each other [Politzer and Murray 1991; Scrocco and Tomasi 1973]. To predict reactive sites of electrophilic and nucleophilic attacks for the investigated molecule, MEP at the B3LYP/SDD optimized geometry was calculated. The negative (red and yellow) regions of MEP were related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity. From the MEP it is evident that the negative charge covers the 17 th Nitrogen group and the positive region is over the Hydrogen group for Quinoline compound. For 6- Nitro quinoline compound electronegative region is over NO_2 and 16th Nitrogen and electropositive region is over Hydrogen and for the 6- Methyl quinoline compound the negative electrostatic potential is over 16th Nitrogen and positive electrostatic potential is over CH_3.





QUINOLINE

6-NITRO QUINOLIE



6-METHYL QUINOLINE

3.1) COMPUTATIONAL DETAILS

Calculations of the title compound are carried out with Gaussian09 program [Frisch *et al.*, 2010] using B3LYP/SDD quantum chemical calculation methods to predict the molecular structure and vibrational wave numbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wave numbers are calculated using the analytic second derivatives to confirm the convergence to minima on the potential surface. The Stuttgart/Dresden effective core potential basis set (SDD) was chosen particularly because of its advantage of doing faster calculations with relatively better accuracy and structures [Hay and Wadt 1985; Zhao and Truhlar 2008]. Then frequency calculations were employed to confirm the structure as minimum points in energy. Parameters corresponding to optimized geometry (SDD) of the title compounds are given in Tables. The absence of imaginary wavenumbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The assignments of the calculated wave numbers are aided by the animation option of GAUSSVIEW program, which gives a visual presentation of the vibrational modes [Dennington *et al.*, 2009].

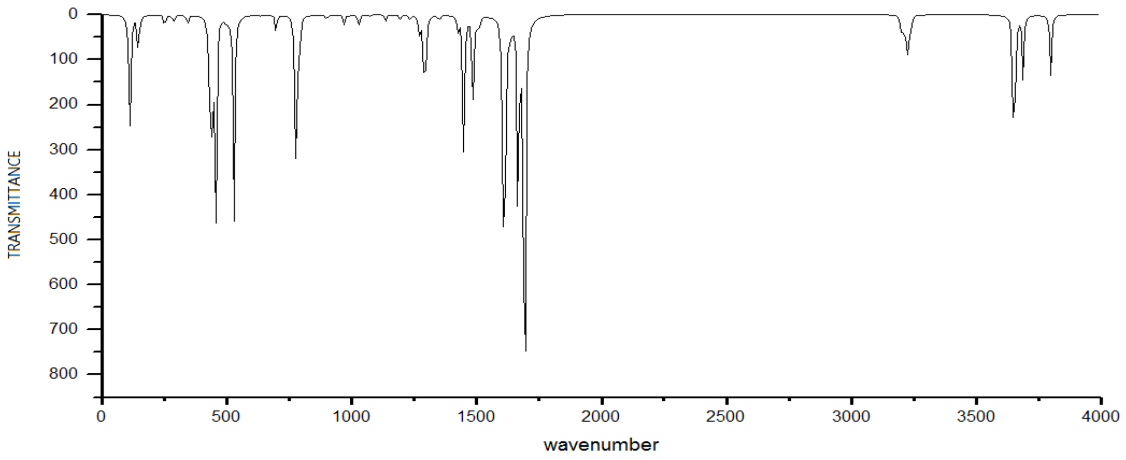
3.2) 1R SPECTRA OF QUINOLINE

(a) TABLE 3.2.1

SERIAL NO	DFT WAVENUMBER	IR SPECTRA WAVENUMBER	ASSIGNMENT
1.	181	182	Yring
2.	189		Yring
3.	379	376	δring
4.	410		YC$_{10}$-H$_7$
5.	490	466	υring
6.	502	508	YC-H
7.	527		υring
8.	531		δring
9.	628	628	δring
10.	658		Yring
11.	761		υring
12.	777	780	Yring
13.	828	827	Yring
14.	831		δring
15.	853	849	υC-N
16.	917		YC-H
17.	950	953	δring
18.	982		YC$_{13}$-H$_{15}$
19.	1010	1004	YC$_1$-H$_8$

20.	1033		Yring
21.	1034		δC-H
22.	1042	1035	YC$_{14}$-H$_{16}$
23.	1051		υring
24.	1143		υC-N
25.	1177	1147	δC$_{1}$-H$_{8}$
26.	1195		δring
27.	1249	1202	δring
28.	1264		δring
29.	1299		δring
30.	1367	1371	δC$_{13}$-H$_{5}$
31.	1414	1412	δC$_{3}$-C$_{4}$
32.	1431		δring
33.	1468		δring
34.	1494	1473	δring
35.	1537		δN$_{17}$-C$_{13}$
36.	1599	1538	δC$_{3}$-C$_{4}$
37.	1634	1620	δ C$_{10}$-H$_{14}$
38.	1669	1672	δC-H
39.	3188		υC$_{2}$-H$_{9}$
40.	3192		υC$_{13}$-H$_{15}$
41.	3199	3199	υC$_{10}$-H$_{17}$
42.	3204		υC-H
43.	3223		υC-H
44.	3235		υC$_{14}$-H$_{16}$
45.	3239	3238	υC-H

In Quinoline the υ C-H stretching vibrational frequencies obtained from DFT are 3223 , 3239 , 3192 , 3199 cm^{-1} and from IR spectrum at 3238 , 3199 cm^{-1} . The υ C-H stretching vibrational frequencies obtained from DFT are 761 , 822 , 527 cm^{-1} and from IR spectrum at 827 cm^{-1} . The υ ring stretching vibrational frequencies obtained from DFT are 3204 , 1051 , 3235 , 3188 , 490 , 527 cm^{-1} and from IR spectrum at 466 cm^{-1} . The υ quinoline stretching vibrational frequencies obtained from DFT are 1143 , 853 cm^{-1} and from IR spectrum at 849 cm^{-1} . The δ C-H bending vibrational frequencies obtained from DFT are 1669 , 1367 , 1177 , 1034 cm^{-1} and from IR spectrum at 1672 , 1371 , 1147 cm^{-1} . The δ C-H quinoline bending vibrational frequencies obtained from DFT are 950 , 379 , 531 cm^{-1} and from IR spectrum at 953 , 376 cm^{-1} . The δ ring bending vibrational frequencies obtained from DFT are 1299 , 1468 , 1494 , 628 , 1195 cm^{-1} and from IR spectrum at 1473 , 628 cm^{-1} . The δ quinoline bending vibrational frequencies obtained from DFT are 1669 , 1634 , 1367 cm^{-1} and from IR spectrum at 1672 , 1620 , 1371 cm^{-1} . The δ C-N bending vibrational frequencies obtained from DFT are 1537 , 1414 cm^{-1} and from IR spectrum at 1412 cm^{-1} . The ϒ C-H symmetric vibrational frequencies obtained from DFT are 502 , 917, 1042 cm^{-1} and from IR spectrum at 508 , 1035 cm^{-1} .



3.3) IR SPECTRA OF 6-NITRO QUINOLINE

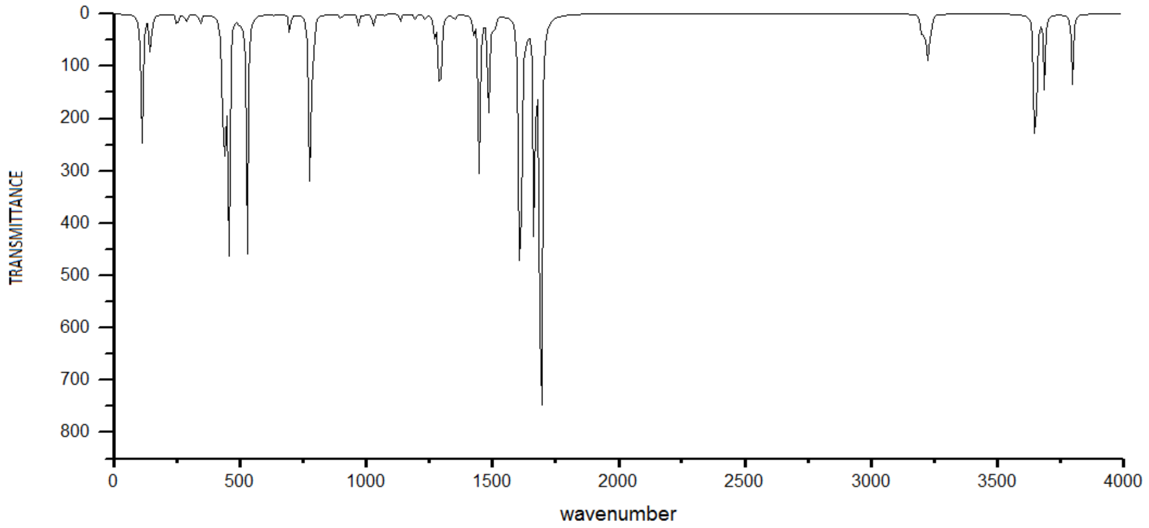
(b) TABLE 3.3.1

SERIAL NO	DFT WAVENUMBER	IR SPECTRA WAVENUMBER	ASSIGNMENT
1.	59		υring
2.	98	95	γring
3.	186		γring
4.	189	190	δN_{17}-O_{18}-O_{19}
5.	264	267	γring
6.	337		υring
7.	376	379	υring
8.	415		γring
9.	495	496	γring
10.	516		γring
11.	531	534	υH_{17}-O_{18}
12.	542		υring
13.	616	616	υC-H
14.	639	638	υring
15.	640		γring
16.	729	728	γring
17.	770	770	υring
18.	773		υN_{17}-O_{18}-O_{19}
19.	818	819	γring
20.	846	849	γC-H
21.	898	895	γC_1-H_7
22.	903		υring
23.	963		υring

24.	974	974	γC_5-H_{10}
25.	997	994	γC-H
26.	1039		γC-H
27.	1046	1046	γC_2-H_8
28.	1050		ʋC_{12}-C_{11}
29.	1104	1106	δC-H
30.	1152	1155	δring
31.	1178	1180	δC-H
32.	1244	1240	δring
33.	1262		δring
34.	1273	1275	Δ$N_{17}O_{19}$-O_{18}
35.	1294	1292	δC-H
36.	1301		δring
37.	1391	1374	δring
38.	1428	1420	δring
39.	1444	1442	δC-H
40.	1465	1469	δC_{12}-H_5
41.	1493	1491	ʋring
42.	1538	1542	ʋring
43.	1602	1606	ʋring
44.	1638	1641	ʋring
45.	1669	1666	ʋring
46.	3202	3204	ʋC_{12}-H_5
47.	3208		ʋC_9-H_{13}
48.	3238		ʋC_5-H_{10}
49.	3239		ʋC_2-H_8
50.	3242	3242	ʋC-H
51.	3265		ʋC_1-C_4

In 6-Nitro quinoline the ʋ C-H stretching vibrational frequencies obtained from DFT are 616 , 3202 , 3208 cm^{-1} and from IR spectrum at 616 , 3204 cm^{-1}. The 6 ʋ ring stretching vibrational frequencies obtained from DFT are 337 , 542 , 639 , 770 , 903 , 963 cm^{-1} and from IR spectrum at 770 cm^{-1}. The ʋ N-O_2 Stretching vibrational frequencies obtained from DFT are 773 , 59 cm^{-1} and from IR spectrum at Nil . The ʋ quinoline stretching vibrational frequencies obtained from DFT are 264 , 1050 , 1493 , 1538 , 1602 , 1638 cm^{-1} and from IR spectrum at 1641 , 1606 , 1542 , 1491 , 267 cm^{-1} . The ʋ C-H quinoline stretching vibrational frequencies obtained from DFT are 3238 , 3265 , 3242 cm^{-1} and from IR spectrum at 3242 $cm^{-1.}$. The δ C-H bending vibrational frequencies obtained from DFT are 1444 , 1294 , 1178 cm^{-1} and from IR spectrum at 1180 , 1292 , 1442 cm^{-1} . The 6 δ ring bending vibrational frequencies obtained from DFT are 376 , 1152 , 1244 , 1262 , 1301 , 1391 cm^{-1} and from IR spectrum at 1374 , 1240 , 1155 , 379 cm^{-1} . The Y C-H symmetric vibrational frequencies obtained from DFT are 846

, 898 , 974 cm^{-1} and from IR spectrum at 849 , 895 , 974 cm^{-1} . The ϒ quinoline symmetric vibrational frequencies obtained from DFT are 1046 , 997 , 1039 cm^{-1} and from IR spectrum at 994 , 1046 cm^{-1} .



3.4) IR SPECTRA OF 6-METHYL QUINOLINE

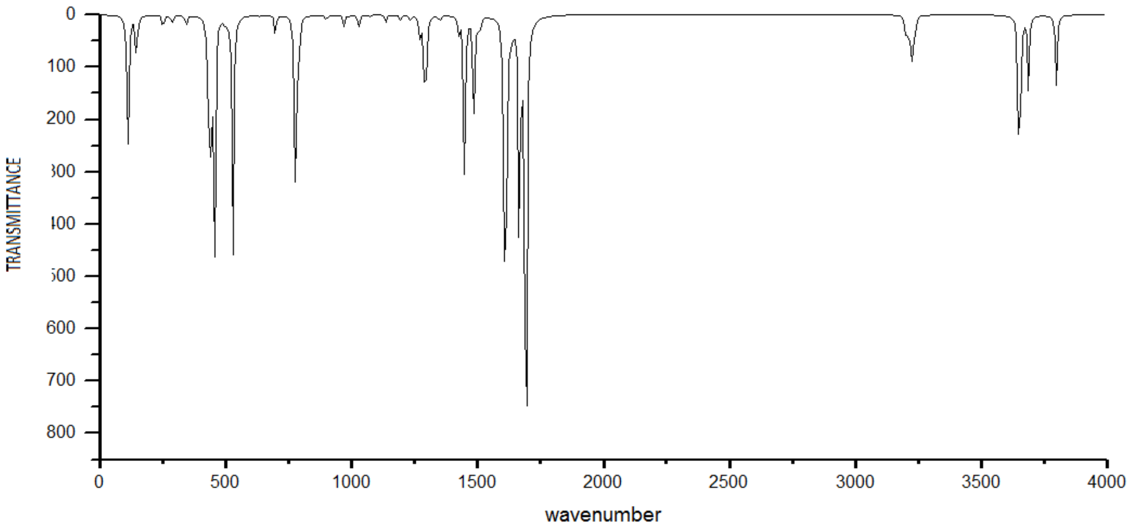
(c) TABLE 3.4.1

SERIAL NO	DFT WAVENUMBER	IR SPECTRA WAVENUMBER	ASSIGNMENT
1.	98		δC_{17}-H_{18}
2.	129	103	υC-H
3.	182	182	γring
4.	269	267	υC-H
5.	292		γring
6.	417	417	γring
7.	417		δring
8.	456		υring
9.	501	504	γring
10.	535	534	γring
11.	542		υring
12.	632		υring
13.	666	633	γring
14.	723		υring
15.	772		υring
16.	808	810	γC-H
17.	844	844	δring
18.	877	874	γC-H

19.	907		υring
20.	933	931	γC_{9}-H_{14}
21.	966		δring
22.	980		γC_{1}-H_{7}
23.	1025	982	γC_{8}-H_{6}
24.	1033		γC-H
25.	1037		υC_{17}-H_{19}
26.	1051	1038	υC_{1}-H_{7}
27.	1088	1086	δring
28.	1145	1146	δring
29.	1176	1176	ΔC_{13}-H_{5}
30.	1211	1210	υC-H
31.	1255		δC_{5}-H_{11}
32.	1272		δring
33.	1302		δC-H
34.	1373	1370	δring
35.	1395	1387	δC-H
36.	1426	1430	δring
37.	1447	1447	υC_{17}-H_{18}
38.	1460		δring
39.	1495	1494	δring
40.	1514		δC_{17}-H_{19}
41.	1521	1521	δC_{17}-H_{20}
42.	1540	1542	υring
43.	1599	1597	υring
44.	1634	1633	δC-H
45.	1679	1674	δring
46.	3036	3040	υC_{17}-H_{19}
47.	3106	3114	υC_{17}-H_{18}
48.	3139	3139	υC_{17}-H_{20}
49.	3185		υC_{9}-H_{14}
50.	3192		υC_{13}-H_{15}
51.	3192		υC-H
52.	3198	3195	υC_{1}-H_{7}
53.	3233		υC-H
54.	3233	3234	υC-H

In 6-Methyl quinoline the ν C-H stretching vibrational frequencies obtained from DFT are 129 , 269 , 3036 cm $^{-1}$ and from IR at 103, 267 , 3040 cm^{-1} . The υ ring stretching vibrational frequencies obtained from DFT are 456 , 542 , 632 , 723 , 772 , 907 cm^{-1} and from IR spectrum at Nil .The υ C-H stretching vibrational frequencies obtained from DFT are 1037 , 1051 , 1447 cm^{-1} and from IR spectrum at 1037, 1447 cm^{-1} . The υ C-H quinoline stretching vibrational frequencies obtained from DFT are 3106 , 3139 , 3198 cm^{-1} and from IR spectrum at 3114 , 3139 , 3195 cm^{-1} . The υ quinoline stretching vibrational frequencies obtained from

DFT are 3185 , 3192 , 3198 , 3233 cm^{-1} and from IR .frequencies obtained from DFT are 98 , 1176 , 1255 cm^{-1} and from IR at 1176 cm^{-1} . The δ ring bending vibrational frequencies obtained from DFT are 417 , 844 , 966 , 1145 , 1272 , 1373 cm^{-1} and from IR at 1370 , 1146 , 844 cm^{-1} . The δ C-H bending vibrational frequencies obtained from DFT are 1302 , 1514 , 1521 cm^{-1} and from IR spectrum at 1521 cm^{-1} . The δ C-H quinoline bending vibrational frequencies obtained from DFT are 1395 , 1634 , 1460 cm^{-1} and from IR spectrum at 1387 , 1633 cm^{-1} . The δ quinoline bending vibrational frequencies obtained from DFT are 1088 , 1426 , 1495 , 1679 cm^{-1} and from IR spectrum at 1674 , 1494 , 1430 , 1086 cm^{-1} . The ϒ C-H symmetric vibrational frequencies obtained from DFT are 933 , 980 , 1025 cm^{-1} and from IR spectrum at 931 , 982 cm^{-1} . The ϒ C-H quinoline symmetric vibrational frequencies obtained from DFT are 417 , 877 , 1033 cm^{-1} and from IR spectrum at 874 , 417 cm^{-1} .



3.5) QUINOLINE OPTIMIZED GEOMETRY

BOND LENGTH (A^{0})

(a) TABLE 3.5.1

C_1-C_2	1.389	C_4-C_{10}	1.4301	C_{13}-C_{14}	1.4303
C_1-C_6	1.4296	C_4-C_5	1.4277	C_{13}-H_{15}	1.0863
C_1-H_8	1.0872	C_5-N_{17}	1.358	C_{13}-N_{17}	1.3362
C_2-C_3	1.4293	C_6-H_{12}	1.0872	C_{14}-H_{16}	1.0859
C_2-H_9	1.0884	H_7-C_{10}	1.088	C_5-H_{11}	1.0858
C_3-C_4	1.4412	C_{10}-C_{14}	1.3881		

BOND ANGLE (^{0})

(b) TABLE 3.5.2

C_2-C_1-C_6	120.3	C_3-C_4-N_{17}	122.1	C_3-C_{10}-C_{14}	119.4
C2-C1-H_8	120.2	C_5-C_4-N_{17}	118.5	H_7-C_{10}-C_{14}	121.0
C_6-C_1-H_8	119.4	C_4-C_5-C_6	120.2	C_{14}-C_{13}-H_{15}	119.9
C_1-C_2-H_9	120.5	C_4-C_5-H_{11}	117.7	C_{14}-C_{13}-N_{17}	123.6
C_3-C_2-H_9	119.0	C_6-C_5-H_{11}	121.9	H_{15}-C_{13}-N_{17}	116.3
C_2-C_3-C_4	119.1	C_1-C_6-C_5	120.4	C_{10}-C_{14}-C_{13}	118.6
C_2-C_3-C_{10}	123.1	C_1-C_6-H_{12}	119.4	C_{10}-C_{14}-H_{16}	121.5
C_4-C_3-C_{10}	117.6	C_5-C_6-H_{12}	120.0	C_{13}-C_{14}-H_{16}	119.5
C_3-C_4-C_5	119.3	C_3-C_{10}-H_7	119.5	C_4-N_{17}-C_{13}	118.1

The optimized molecular structure of Quinoline was determined by using Gaussian09 program. The bond lengths are C_4-N_{17} 1.358 (A0) ,C_{13}-N_{17} 1.3362 (A0) . Bond angles are C_3-C_4-N_{17} 122.1 (0) , C_5-C_4- N_{17} 118.5 (0), C_{14}-C_{13}-N_{17} 123.6 (0) , H_{15}-C_{13}-N_{17} 116.3 (0) , C_4-N_{17}-C_{13} 118.1 (0)

3.6) 6-NITRO QUINOLINE OPTIMIZED GEOMETRY

BOND LENGTH (A^0)

(a) TABLE 3.6.1

C_1-C_2	1.3852	C_5-H_{10}	1.0854
C_1-C_6	1.4256	C_6-N_{17}	1.4775
C_1-H_7	1.0837	C_9-C_{11}	-1.3869
C_2-C_3	1.4291	C_9-H_{13}	- 1.0873
C_2-H_8	1.085	C_{11}-C_{12}	-1.431
C_3-C_4	1.4424	C_{11}-H_{14}	1.0854
C_3-N_{16}	1.3825	C_{12}-H_{15}	1.0878
C_4-C_5	1.4232	C_{12}-N_{16}	1.337
C_4-C_9	1.4307	N_{17}-O_{18}	1.28
C_5-C_6	1.3876	N_{17}-0_{19}	1.2791

BOND ANGLE (^{0})

(b) TABLE 3.6.2

C_2-C_1-C_6	118.7	C_4-C_5-C_9	122.7	C_9-C_{11}-H_{14}	121.5
C_2-C_1-H_7	122.0	C_4-C_5-C_6	118.9	C_{12}-C_{11}-H_{14}	119.5
C_6-C_1-H_7	119.1	C_4-C_5-H_{10}	121.1	C_{11}-C_{12}-H_{15}	119.9

C_1-C_2-C_3	120.7	C_6-C_5-H_{10}	119.9	C_{11}-C_{12}-N_{16}	123.7
C_1-C_2-H_8	121.6	C_1-C_6-C_5	122.6	H_{15}-C_{12}- N_{16}	116.2
C_3-C_2-H_8	117.5	C_1-C_6-N_{17}	118.6	C_3-N_{16}-C_{12}	118.0
C_2-C_3-C_4	119.4	C_5-C_6-N_{17}	118.7	C_6-N_{17}-0_{18}	118.3
C_2-C_3-N_{16}	118.5	C_4-C_9-C_{11}	119.1	C_6-N_{17}-O_{19}	117.9
C_4-C3-N_{16}	122.0	C_4-C_9-H_{13}	119.6	O_{18}-N_{17}-O_{19}	123.7
C_3-C_4-C_5	119.3	C_{11}-C_9-H_{13}	121.1		
C_3-C_4-C_9	117.9	C_9-C_{11}-C_{12}	118.9		

The optimized molecular structure of 6-Nitro quinoline was determined by using Gaussian09 program. The bond lengths are C_3-N_{16} 1.3825 (A0) ,C_6-N_{17} 1.4775 (A0), C_{12}-N_{16} 1.337 (A0) , N_{17}-O_{18} 1.28 (A0) , N_{17}- O_{19} 1.2791 (A0) . Bond angles are C_2-C_3-N_{16} 118.5 (0) , C_4 -C_3-N_{16} 122 (0), C_1-C_6-N_{17} 118.6 (0) , C_5-C_6-N_{17} 118.7 (0) , C_{11}-C_{12}-N_{16} 123.7 (0) , H_{15}-C_{12}-N_{16} 116.2 (0) , C_3-N_{16}-C_{12} 118 (0) , C_6-N_{17}-O_{18} 118.3 (0) , C_6-N_{17}- 0_{19} 117.9 (0) , O_{18}-N_{17}-0_{19} 123.7 (0) .

3.7) 6-METHYL QUINOLINE OPTIMIZED GEOMETRY

BOND LENGTH (A^0)

(a) TABLE 3.7.1

C_1-C_5	1.4295	C_3-C_9	1.4297	C_9-H_{14}	1.089
C_1-H_7	1.0881	C_4-C_5	1.3889	C_{12}-C_{13}	1.4362
C_1-N_{16}	1.3369	C_4-H_{10}	1.088	C_{12}-C_{17}	1.5168
C_2-C_3	1.4404	C_5-H_{11}	1.0861	C_{13}-H_{15}	1.0886
C_2-C_8	1.428	H_6-C_8	1.086	C_{17}-H_{18}	1.0988
C_2-N_{16}	1.3839	C_8-C_{13}	1.3867	C_{17}-H_{19}	1.0988
C_3-C_4	1.4294	C_9-C_{12}	1.3912	C_{17}-H_{20}	1.0956

BOND ANGLE (^{0})

(b) TABLE 3.7.2

C_5-C_1-H_7	120.0	C_1-C_5-C_4	118.9	C_8-C_{13}-C_{12}	121.5
C_5-C_1-N_{16}	123.5	C_1-C_5-H_{11}	119.5	C_8-C_{13}-H_{15}	119.7
H_7-C_1-N_{16}	116.4	C_4-C_5-H_{11}	121.4	C_{12}-C_{13}-H_{15}	118.7
C_3-C_2-C_8	118.4	C_2-C_8-H_{16}	117.7	C_1-N_{16}-C_2	118.0
C_3-C_2-C_8	122.3	C_2-C_8-C_{13}	120.3	C_{12}-C_{17}-H_{18}	111.1
C_8-C_2-N_{16}	118.8	H_6-C_8-C_{13}	121.8	C_{12}-C_{17}-H_{19}	111.1
C_2-C_3-C_4	117.5	C_3-C_9-C_{12}	121.3	C_{12}-C_{17}-H_{20}	111.6
C_2-C_3-C_9	119.3	C_3-C_9-H_{14}	118.6	H_{18}-C_{17}-C_{19}	107.0

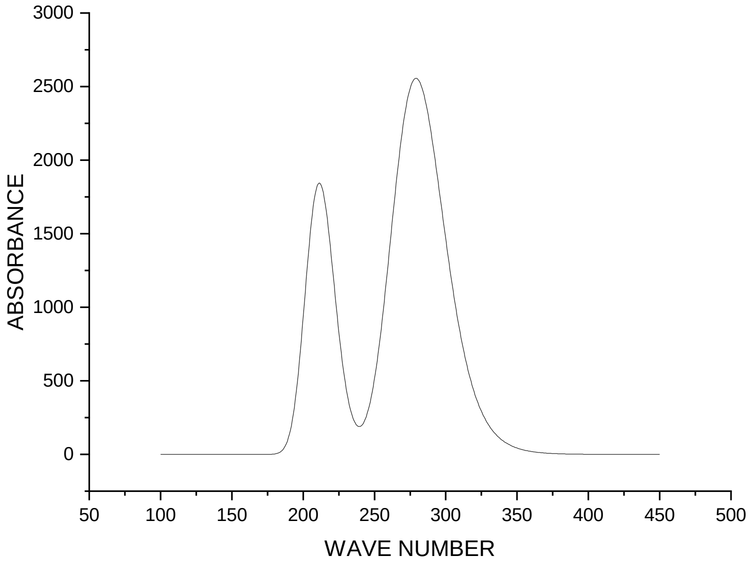
C_4-C_3-C_9 123.1	C_{12}-C_9-H_{14} 119.9	H_{18}-C_{17}-H_{20} 107.8
C_3-C_4-C_5 119.4	C_9-C_{12}-C_{13} 118.6	H_{19}-C_{17}-H_{20} 107.8
C_3-C_4-H_{10} 119.5	C_9-C_{12}-C_{17} 121.7	
C_5-C_4-H_{10} 120.9	C_{13}-C_{12}-C_{17} 119.5	

The optimized molecular structure of 6-Methyl quinoline was determined by using Gaussian09 program. The bond lengths are C_1-N_{16} 1.3369 (A0) , C_2-N_{16} 1.3839 (A0) . Bond angles are C_5-C_1-N_{16} 123.5 (0) , H_7-C_1-N_{16} 116.4 (0) , C_8-C_2-N_{16} 118.8 (0) , C_1-N_{16}-C_2 118 (0)

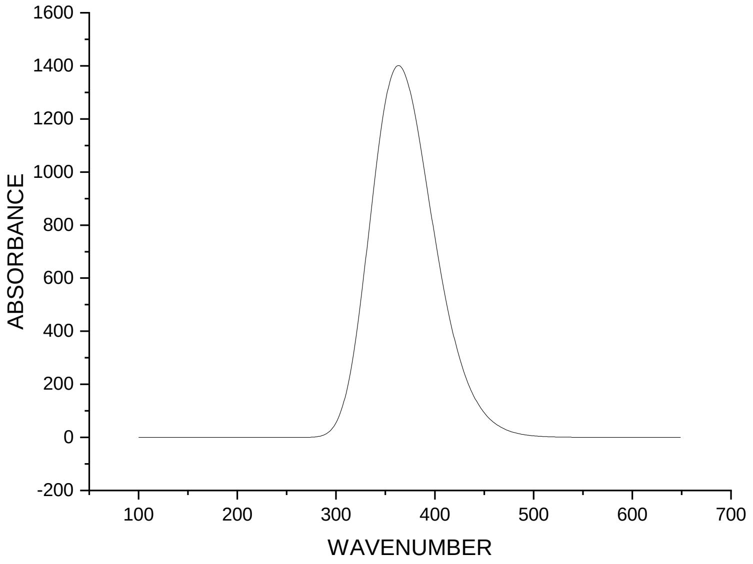
3.8) UV-VIS SPECTRA

The UV–vis spectra for the compounds in ethanol solvent were calculated by TDSCF/B3LYP/SDD level of calculation . The obtained theoretical UV–vis absorption spectra were presented in figures. As can be seen the position of the absorption bands is influenced by the structure of compounds. Quinoline shows two absorption bands at 279.9832 and 212.09778 The substitution of Nitro group resulted in the shift of the absorption peak to 366.1721 whereas the substitution of Methyl group resulted in a peak at 282.61596 .

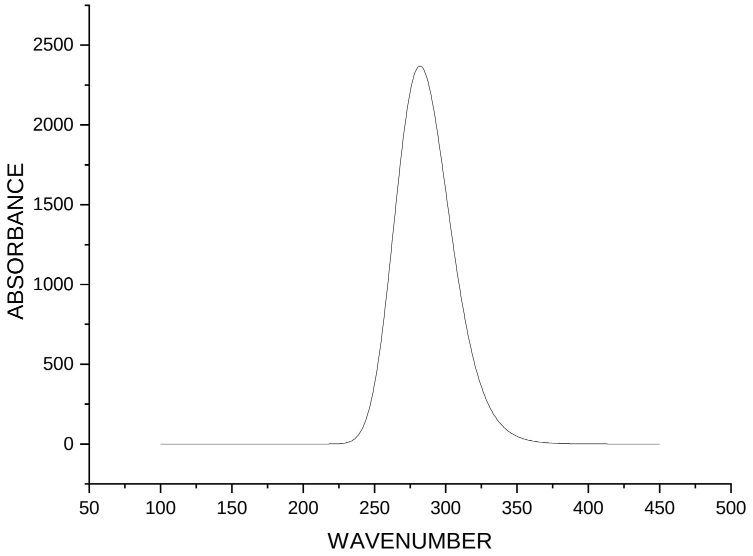
3.8.1 UV SPECTRA OF QUINOLINE



3.8.2) UV SPECTRA OF 6-NITRO QUINOLINE



3.8.3) 6-METHYL QUINOLINE



3.9) DIPOLE MOMENT & FIRST HYPER POLARAIZABILITY

All symmetric molecules have zero dipole moment. The dipole moment of a molecule signifies the deviation from symmetry of a molecule. The Quinoline molecule has a dipole moment of 2.5468 D, 6-Methyl Quinoline has 2.792 D and 6-Nitro quinoline has 5.264 D.

In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a 3×3×3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes

$$E = E_0 - \sum_i \mu_i F^i - \frac{1}{2}\sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6}\sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24}\sum_{ijkl} \gamma_{ijkl} F^i F^j F^k F^l + \ldots$$

where E_0 is the energy of the unperturbed molecule, F^i is the field at the origin, μ_i, α_{ij}, β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability, the first hyperpolarizability, and second hyperpolarizability, respectively.

$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$

where,

$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$

$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$

$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$

Urea is considered as a standard NLO material because it has the advantage of corresponding to a molecule that contains classical organic atoms and both single and double bonds. Its hyperpolarizabilty is 0.13×10^{-30} esu.

In the case of Quinoline, the β_0 was calculated to be 1.4×10^{-30} esu. With the substitution of Methyl group the value was decreased to 1.12×10^{-30} esu and there was a ten times increase in the value with the substitution of Nitro group in the same position as that of the Methyl group. Thus it is seen that the substitution of a strong electron acceptor group increases the first hyperpolarizability value. These values of hyperpolarizability shows molecule with large dipole moment exhibit large hyperpolarizability values.

CHAPTER 4

CONCLUSION

Quinoline compounds widely used in the manufacture of dyes, production of other speciality chemicals and as a solvent for resins and terpenes. The theoretical and experimental comparative studies of these compounds are important to understand the nature, property, and applicability.

Quinoline , 6-Methyl Quinoline and 6-Nitro Quinoline were theoretically studied using Gaussian09 program. The geometry optimization of the title compounds were carried out using DFT using B3LYP/SDD. The donor and acceptor substitution effect on the vibrational spectra of the compounds were studied. The change in the geometrical parameters with substitution also were studied. The HOMO-LUMO energy gap and the UV-VIS spectral studies on the compound proves these compounds have potential to be used in OLED devices, as they show absorption in the UV region. As the β value is related to the second order susceptibility the calculated dipole moment and first hyperpolarizability values shows these compounds could be used in NLO devices particularly for second harmonic generation. The molecular electrostatic potential plot of these molecules shows the electronegative and electropositive sites , which is crucial for substrate binding.

FIELDS OF APPLICATION

- OLED - Organic Light Emitting Diode
- Non Linear optical material

FUTURE STUDIES

- Raman spectra and SERS studies can be performed
- Photoluminescent spectral studies
- Molecular docking studies would reveal the behaviour of these compounds against pathogens.
- Second hyperpolarizability calculations could disclose the third order susceptibility

REFERENCES

1) Arafa, R.K.; Hegazy, G.H.; Piazza, G.A.; Abadi, A.H. “Synthesis and in vitro antiproliferative effect of novel quinoline-based potential anticancer agents”, Eur. J. Med. Chem. 63, 2013, 826-832.

2) Arslan, H.; Florke, U.; Kulcu, N.; Binzet, G. “The molecular structure and vibrational spectra of 2-chloro-N-(diethylcarbamothioyl) benzamide by Hartree-Fock and density functional methods”, Spectrochim. Acta 68, 2007, 1347-1355.

3) Aruldas, G. “Molecular Structure and Spectroscopy”, PHI Learning Pvt. Ltd, New Delhi, 2004.

4) Arunagiri, C.; Arivazhagan, M.; Subashini, A. “Vibrational spectroscopic (FT-IR and FT-Raman), first-order hyperpolarizability, HOMO, LUMO, NBO, Mulliken charges and structure determination of 2-bromo-4-chlorotoluene” Spectrochim. Acta Part A 79, 2011, 1747-1756. 184.

5) Asiri, A.M.; Baglaf, A.O.; Rahman, R.M.A.; Khan, S.A.; Ishaq, M. “Synthesis and Spectroscopic Studies of Ru(II) Complexes of 1,2,4-Triazoles, 1,2,4-Triazines and Pyrimidine Derivatives”, Asian J. Chem. 25, 2013, 7779-7782.

6) Bellamy, L.J. “The IR spectra of complex molecules”, John Wiley & sons, New York 1975.

7) Bernstein, M.P.; Mattioda, A.L.; Sandford, S.A.; Hudgins, D.M. “Laboratory Infrared Spectra of Polycyclic Aromatic Nitrogen Heterocycles: Quinoline and Phenanthridine in Solid Argon and H2O”, Astrophys.J, 626, 2005, 909-918.

8) Bonnenfant, S.; Thomas, C.M.; Vita, C.; Subra, F.; Deprez, E.; Zouhiri, F.; Desmaële, D.; D'Angelo, J.; Mouscadet, J.F.; Leh, H. “Styrylquinolines, Integrase Inhibitors Acting Prior to Integration: a New Mechanism of Action for Anti-Integrase Agents ”, J. Virol. 78, 2004, 5728-5736.

9) Boyd, R.W. “Nonlinear Optics”, Elsevier, USA, 2003.

10) Brown, R.D.; Harcourt, R.D. “A theoretical treatment of the chemistry of quinoline”, J. Chem. Soc., 1959, 3451-3460.

11) Camargo, A.J.; Napolitano, H.B.; Zukerman-Schpector, J.; “Theoretical investigation of the intramolecular hydrogen bond formation, non-linear optic properties and electronic absorption spectra of the 8-hydroxiquinoline”, J. Mol. Struct. (Theochem.) 816, 2007, 145-151. 185.

12) Chauhan, P.M.S.; Srivastava, S.K. “Present Trends and Future Strategy in Chemotherapy of Malaria”, Curr. Med. Chem. 8, 2001, 1535-1542.

13) Chen, C.H.; Shi, J.M. “Metal chelates as emitting materials for organic electroluminescence”, Coord. Chem. Rev. 171, 1998, 161-174.

14) Chou , P.T.; Chen,Y.C.; Yu,W.S.; Chou,Y.H.; Wei,C.Y.; Cheng,Y.M. “Excited-State Intramolecular Proton Transfer in 10-Hydroxybenzo[h]quinoline”, J. Phys. Chem. A 105, 2001, 1731-1740.

15) Chou, P.T.; Wei, C.Y. “Photophysics of 10-Hydroxybenzo [h] quinoline in Aqueous Solution”, J. Phys. Chem. 100, 1996, 17059-17066.

16) Cisek, R.; Spencer, L.; Prent, N.; Zigmantas, D.; Espie, G.; Barzda,V. “Optical microscopy in photosynthesis”, Photosynth. Res.102, 2009, 111-141.

17) Coates, J. “Encyclopedia of Analytical Chemistry: Interpretation of Infrared spectra, A Practical Approach”, John Wiley and Sons, Chichester, 2000. 186 .

18) Colthup, N.B.; Daly, L.H.; Wiberly, S.E. “Inroduction to Infrared and Raman Spectroscopy”, third ed., Academic Press, Boston, 1990.

19) Cones, J.; Cones, P. “Near-Infrared Planetary Spectra by Fourier Spectroscopy”, J. Opt. Soc. Am. 56, 1966, 896-910.

20) Credo, G.M.; Winn, D.L.; Buratto, S.K. “Near-Field Scanning Optical Microscopy of Temperature and Thickness-Dependent Morphology and Fluorescence in Alq 3 Films”, Chem. Mater. 13, 2001, 1258-1265.

21) Crookell, A.; Hendra, P.J.; Mould, H.M.; Turner, A.J. “Fourier transform Raman spectroscopy in the near-infrared region”, J. Raman Spectrosc. 21, 1990, 85-90.

22) Cutleer, D.J. “The Development of Fourier Transform Raman Spectroscopy”, Spectrochim. Acta 46 A, 1990, 123-129.

23) Dorn, A.; Vippagunta, S.R.; Matile, H.; Jaquet, C.; Vennerstrom, J. L.; Ridley, R. G. “An assessment of drug-haematin binding as a mechanism for inhibition of haematin polymerisation by quinoline antimalarials”, Biochem.Pharmacol. 55, 1998, 727-736.

24) Dunning Jr., T.H. “Gaussian basis sets for use in correlated molecular calculations. I.The atoms boron through neon and hydrogen”, J. Chem. Phys. 90, 1989, 1007-1023.

25) Eaton, D.F. “Nonlinear optical materials” Science, 253, 1991, 281-287.

44) El-Shahway, A.S.; Ahmed, S.M.; Sayed, N.K.; “INDO/SCF-CI calculations and structural spectroscopic studies of some complexes of 4-hydroxyacetanilide”, Spectrochim.Acta. 66 A, 2007, 143-152.

26) Epstein, A.J.; “Electrically Conducting Polymers: Science and Technology”, Mater. Res. Soc. Bull. 22, 1997, 16-23. 187.

27) Famin, O.; Krugliak, H.; Ginsberg, H.; “Kinetics of inhibition of glutathione-mediated degradation of ferriprotoporphyrin IX by antimalarial drugs”, Biochem. Pharmacol.58, 1999, 59-68.

28) Ferlin, M.G.; Gatto, B.; Chiarelotto, G.; Palumbo, M. “Pyrrolo-quinoline derivatives as potential antineoplastic drugs”, Bioorg. Med. Chem. 8, 2000, 1415-1422.

29) Foresman, J.B. “Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian”, Gaussian, Inc., Pittsburg, 1996.

30) Francl, M.M.; Binkley, J.S.; Gordon, M.S.; DeFrees, D.J.; Pople, J.A. “Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row element”, J. Chem. Phys. 77, 1982, 3654-3665.

31) Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J.A. Jr.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K.N.;Staroverov, V.N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J.M.; Klene, M.; Knox, J.E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A.J.;Cammi, R.; Pomelli, C.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A.D.; Farkas, O.; Foresman, J.B.; Ortiz, J.V.; Cioslowski, J.; Fox ,M. “Gaussian 09, Revision B.01”, Gaussian, Inc., Wallingford CT, 2010.

32) Fukui, K. “Role of Frontier Orbitals in Chemical recactions”, Science 218, 1982, 747- 754.

33) Gadre, S.R.; Shirsat, R.N. “Electrostatics of Atoms and Molecules”, Universities Press, Hyderabad, India, 2000. 188.

34) Garito, A.; Shi, R.; Wu, M.; “Non-Linear Optics of Organic and Polymer Materials”, Physics Today, 1994, p51-57.

35) Glendening, E.D.; Reed, A.E.; Carpenter, J.E.; Weinhold, F. NBO Version 3.1, TCI, University of Wisconsin, Madison, 1998.

36) Go, M.; Ngiam, T.; Tan, A.L.; Kuaha, K.; Wilairat, P. “Structure-activity relationships of some indolo[3,2-c]quinolines with antimalarial activity”, Eur. J. Pharm. Sci. 6, 1998, 19-26.

37) Griffiths, P.R.; De Haseth J.A. “Fourier Transform Infrared Spectroscopy”, Wiley, New York, 1986.

38) Hay, P.J.; Wadt, W.R. “Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg”, J. Chem. Phys. 82, 1985, 270-283.

39) Hayat, F.; Salahuddin, A.; Umar, S.; Azam, A. “Synthesis, characterization, antiamoebic activity and cytotoxicity of novel series of pyrazoline derivatives bearingquinoline tail”, Eur. J. Med. Chem. 45, 2010, 4669-4675.

40) He, Z.; Milburn, G.H.W.; Baldwin, K.J.; Smith, D.A.; Danel, A.; Tomasik, P. “The efficient blue photoluminescence of pyrazolo-[3,4-b]-quinoline derivatives and the energy transfer in polymer matrices”, J. Lumin. 86, 2000, 1-14.

41) Hirschfeld, T.; Chase, B. “FT-Raman Spectroscopy: Development and Justification”, Appl. Spectrosc. 40, 1986, 133-137.

42) Hollas, J.M. “Modern spectroscopy”, 4th edition, John Wiley and sons, England, 2004.

43) Holtje, H.D.; Sippl, W.; Rognan, D.; Folkers, G. “Molecular Modeling- Basis Principles and Applications”, Wiley-VCH, England, 2003.

44) Inkaya, E.; Gunnaz, S.; Ozdemir, N.; Dayan, O.; Dinçer, M.; Cetinkaya, B. “QuantumChemical, IR, NMR and X-ray Diffraction Studies on 2,6-Bis(1-benzyl-1Hbenzo[d]imidazol-2-yl)pyridine”, Sepctrochim. Acta Part A 103, 2013, 255-263.

45) Ismail, F.M.D.; Dascombe, M.J.; Carr, P.; Merette, S.; Rouault, P. "Novel Aryl-bis-quinolines with Antimalarial Activity In-vivo", J. Pharm. Pharmacol. 50, 1998, 483-492.

46) Jain, V.K. "Introduction to Atomic and molecular Spectroscopy", Narosa, New Delhi, 2011. 189.

47) Jampilek, J.; Musiol, R.; Pesko, M.; Kralova, K.; Vejsova, M.; Carroll, J.; Coffey, A.; Finster, J.; Tabak, D.; Niedbala, H.; Kozik, V.; Polanski, J.; Csollei, J.; Dohnal, J. "Ring-substituted 4-Hydroxy-1H-quinolin-2-ones: Preparation and Biological Activity", Molecules 14, 2009, 1145-1159.

48) Jampilek, J.; Dolezal, M.; Kunes, J.; Buchta, V. The 8th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-8), November 1-30, 2004 Basel, Switzerland.

49) Janczarek, I.F.; Gondek, E.; Kityk, I.V.; Danel, K.; Krzeminska , L.; Sanetra , J.; Kwiecien, B. "Optical spectra of some 6-styrylo-1H-pyrazolo[3,4-b]quinolines", Spectrochimica Acta 63 A, 2006, 320-329.

50) Jankowski, K.; Becherer, R.; Scharf, P.; Schiffer, H.; Ahlrichs, R. "The impact of higher polarization basis functions on molecular ab initio results", J. Chem. Phys. 82, 1985, 1413-1419.

51) Kleinman, D.A. "Nonlinear dielectric polarization in optical media", Phys. Rev. 126, 1962, 1977-1979.

52) Kohn, W.; Sham, L.J. "Self-Consistent Equations Including Exchange and Correlation Effects", Phys. Rev. 140, 1965, 1133-1138.

53) Kolinsky, P.V. "New materials and their characterization for photonic device applications" Opt. Eng. 31, 1992, 1676-1684.

54) Koopmans, T. "Uber die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms", Physica 1, 1934, 104-113. 190.

55) Kosar, B.; Albayrak, C. "Spectroscopic investigations and quantum chemical computational study of (E)-4-methoxy-2-[(p-tolylimino) methyl] phenol", Spectrochim. Acta A 78, 2011, 160-167.

56) Krishnakumar, V.; Prabavathi, N.; Muthunatesan, S. "Density functional theory calculations and vibrational spectra of 6-methyl 1,2,3,4-tetrahyroquinoline", Spectrochim. Acta. 69, 2008, 853-859.

57) Krishnan, R.; Binkley, J.S.; Seegar, R.; Pople, J.A. "Self-consistent orbital methods. XX. A basis set for correlated wave functions", J. Chem. Phys. 72, 1980, 650-654.

58) Kriz, P. L. "Introduction to Spectroscopy", John Wiley, New York, III Edition, 2003.

59) Kubicki, M.; Borowiak, T.; Antkowiak,W.Z. "10-Hydroxybenzo [h]quinoline", Acta Cryst. C: Cryst. Struct.Commun. 51, 1995, 1173-1175.

60) Kuhn, H. "Free electron model for absorption spectra of organic dyes", J.Chem. Phys. 16, 840-841, 1948.

61) Kulkarni, A. P.; Tonzola, J.; Babel, A.; Jenekhe, S.A. “Electron transport materials for organic light-emitting diodes”, Chem. Mater. 16, 2004, 4556-4573.

62) Kumru, M.; Küçük, V.; Akyürek, P. “Vibrational spectra of quinoline-4-carbaldehyde: Combined experimental and theoretical studies”, Spectrochim. Acta 113 A, 2013, 72- 79.

63) Kuzmnay, H. “Solid Spectroscopy”, Springer, New York, 1998.

64) Kuzyk, M.G.; Kenneth D.; Stegeman, G.I. “Theory of Molecular Nonlinear Optics”, Advances in Optics and Photonics 5, 2013, 4-82.

65) Larsson, S. “Chemical Physics”, CRC Press, USA, 2012. 191.

66) Le-Gourrierec, D.; Kharlanov, V.; Brown, R.G.; Rettig, W. “Excited-state intramolecular proton-transfer (esipt) in 2-(2'-hydroxyphenyl) pyridine and some carbon-bridged derivatives”, J. Photochem. Photobiol. A: Chem. 117, 1998, 209-216.

67) Lewars. E.G. “Computational Chemistry”, Springer, USA, 2011.

68) Lewis, D.F.V.; Loannides, C.; Parke, D.V. “Interaction of a series of nitriles with the alcohol-inducible isoform of P450: Computer analysis of structure-activity relationships”, Xenobiotica 24, 1994, 401-408.

69) Louran,G.; Lapkowski, M.; Quillard, S.; Pron, A.; Buisson, J.B.; Lefrant, S. “Vibrational Properties of Polyaniline-Isotope Effects ”, J. Phys. Chem. 100, 1996, 6998-7006.

70) Luque, F.J.; Lopez, J.M.; Orozco, M. “Perspective on Electrostatic interactions of a solute with a continuum. A direct utilization of ab initio molecular potentials for the prevision of solvent effects,” Theor. Chem. Acc. 103, 2000, 343-345.

71) Pinedo, H.M. “Camptothecins: New Anticancer Agents”, CRC Press, Boca, Raton, 1995.

72) Mac Diarmid, A.G.; Epstein, A.J. “Photonic and Optoelectronic Polymers”, American Chemical Society, Washington, DC, 1997.

73) Maguire, M.P.; Sheets, K.R.; K. Mcvety, K.; Spada, A.P.; Zilberstein, A. “A New Series of PDGF Receptor Tyrosine Kinase Inhibitors: 3-Substituted Quinoline Derivatives”, J. Med. Chem. 37, 1994, 2129-2137.

74) Martin, J.M.L.; Alsenoy, C.V. “GAR2PED, A Program to obtain a Potential Energy Distribution from a Gaussian archive record”, University of Antwerp, Belgium, 2007.

75) Martinez, M.L.; Cooper, W.C.; Chou, P.T.; “A novel excited-state intramolecular proton transfer molecule, 10-hydroxybenzo [h]quinoline”, Chem. Phys. Lett. 193, 1992, 151-154.

76) Mary, Y.S.; Panicker, C.Y.; Varghese, H.T.; Raju, K.; Bolelli, T.E.; Yildiz, I.; Granadeiro, M.C.; Nogueira.H.I.S. “Vibrational spectroscopic studies and computational study of 4-fluoro-N-(2′-hydroxy-4′-nitrophenyl)phenylacetamide”, J.Mol. Struct. 994, 2011, 223-231. 192.

77) Mary, Y.S.; Varghese, H.T.; Panicker , C.Y.; Ertan, T.; Yildiz, I.; Temiz-Arpaci, O. “Vibrational spectroscopic studies and ab initio calculations of 5-nitro-2-(pfluorophenyl)benzoxazole”, Spectrochim. Acta. 71, 2008, 566-571.

78) Mary, Y.S.; Varghese, H.T.; Panicker, C.Y.; Dolezal, M. “Vibrational spectroscopic studies and ab initio calculations of a substituted amide of pyrazine-2-carboxylic acid - C12H10ClN3O”, Spectrochim. Acta. 71, 2008, 725-730.

79) Matsumiya, H.; Hoshino, H.; “Selective Determination of Beryllium(II) Ion at Picomole per Decimeter Cubed Levels by Kinetic Differentiation Mode Reversed Phase High-Performance Liquid Chromatography with Fluorometric Detection Using 2-(2Hydroxyphenyl)-10-hydroxybenzo[h]quinoline as Precolumn Chelating Reagent”, Anal. Chem. 75, 2003, 413-419.

80) Matsumiya, H.; Hoshino, H.; Yotsuyanagi, T. “A novel fluorescence reagent, 10-hydroxybenzo[h]quinoline-7-sulfonate, for selective determination of beryllium(II) ion at pg cm−3 levels”, Analyst 126, 2001, 2082-2086.

81) Mile, C.; Guiliano, M.; Reymond, H.; Dou, H. “Analysis of Hydrocarbons by Fourier Transform Infrared Spectroscopy”, Intern. J. Environ. Anal. Chem. 21, 1985, 239-250.

82) Minitha, R.; Mary, Y.S.; Varghese, H.T.; Panicker, C.Y.; Ravindran, R.; Raju, K.; Nair, V.M. “FT-IR, FT-Raman and computational study of 1H-2,2-dimethyl-3Hphenothiazin-4[10H]-one”, J. Mol. Struct. 985, 2011, 316-322.

83) Mousnier, A.; Leh, H.; Mouscadet, J.F.; Dargemont, C. “Nuclear Import of HIV-1 Integrase Is Inhibited in Vitro by Styrylquinoline Derivatives”, Mol. Pharmacol. 66, 2004, 783-788.

84) Mulliken, R.S. “Electronic Population Analysis on LCAO-MO Molecular Wave Functions”, J. Chem. Phys. 23, 1955, 1833-1840.

85) Musiol, R.; Podeszwa, B.; Finster, J.; Niedbala, H.; Polanski, J. “An efficient microwave-assisted synthesis of structurally diverse styrylquinolines”, Monatsh.chem 137, 2006, 1211-1217.

86) Nakamoto, K. “Infrared and Raman Spectrum of Inorganic and coordination Compounds”, 5th ed., John Wiley and Sons, Inc., New York, 1997.

87) Neu, H.C. “Quinolone Antimicrobial Agents”, Annual Rev. Med. 43, 1992, 465-486. 193.

88) Nie, W.J. “Optical Nonlinearity: Phenomena, applications, and materials”, Adv. Mater. 5, 1993, 520-545.

89) Niziol, J.; Danel, A.; Boiteux, G.; Davenas, Jarosz, J.B.; Wisla, A.; Seytre, G. “Optical properties of new pyrazolo[3,4-b]quinoline and its composites”, Synth. Met. 127, 2002, 175-180.

90) Palmer, M.H.; in: “The Structure and Reactions of Heterocyclic Compounds”, Edward Arnold Publisher Ltd., London, 1967.

91) A.K.; Alsenoy, C.V. “Ab initio and density functional theory studies on vibrational spectra of 3-{[(4-methoxyphenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one”, Eur. J. Chem. 1, 2010, 37-43.

92) Park, J.; Park, J.S.; Park, Y.G.; Lee, J.Y.; Kang, J.W.; Liu, J.; Dai, L.; Jin, S.H. “Synthesis, characterization of the phenylquinoline-based on iridium(III) complexes for solution

processable phosphorescent organic light-emitting diodes", Organic Electronics 14, 2013, 2114-2123.

93) Parker, S.E.; Williams, K.; Turner, A.J.; Hendra, P.J. "Fourier Transform Raman Spectroscopy Using a Bench-Top FT-IR Spectrometer", Appl. Spectros. 42, 1988, 796- 800.

94) Parr, R.G.; Yang, W. "Density Functional Theory of Atoms and Molecules" Oxford, New York, 1989.

95) Parr, R.J.; Pearson, R.G. "Absolute hardness: comParrion parameter to absolute electronegativity", J. Am. Chem. Soc. 105, 1983, 7512-7516. 194.

96) Parr, R.J.; Szentpaly, L.V.; Liu, S. "Electrophilicity Index", J. Am. Chem. Soc. 121, 1999, 1922-1924.

97) Podeszwa, B.; Niedbala, H.; Polanski, J.; Musiol, R.; Tabak, D.; Finster, J.; Serafin, K.; Richardson, D.R. "Investigating the antiproliferative activity of quinoline-5,8- diones and styrylquinolinecarboxylic acids on tumor cell lines", Bioorg. Med. Chem. Lett. 17, 2007, 6138-6141.

98) Politzer, P.; Murray, J. S. "in: Theoretical Biochemistry and Molecular Biophysics: A Comprehensive Survey", Adenine Press, Schenectady, NY, 1991.

99) Pucci, M.J.; Wiles, J.A. "Bacterial Topoisomerase Inhibitors: Quinolones and Beyond", In Antimicrobials, Springer, ch.16, pp. 307-326, 2014.

100) Purohit, G.; Joshi, G.C.; "Second-order polarizabilities of some quinolines", Indian J. Pure Appl. Phys. 41, 2003, 922-927.

101) Raj, B.N.B.; Kurup, M.R.P.; Suresh, E. "Synthesis, spectral characterization and crystal structure of N-2-hydroxy-4-methoxybenzaldehyde-N′-4-nitrobenzoyl hydrazone and its square planar Cu(II) complex", Spectrochim. Acta 71, 2008, 1253- 1260.

102) Ramachandran, K.I.; Deepa, G.; Namboori, K. "Computational Chemistry and Molecular Modelling: Principles and Applications", Springer, 2008.

103) Roberts, E.L.; Chou, P.T.; Alexander,T.A.; Agbaria, R.A.; Warner,I.M. "Effects of Organized Media on the Excited-State Intramolecular Proton Transfer of 10-Hydroxybenzo[h]quinoline", J. Phys. Chem. 99, 1995, 5431-5437.

104) Roeges, N.P.G. "A guide to the complete interpretation of IR spectra of Organic Compounds", Wiley, New York, 1994.

104) Sathyanarayana, D.N. "Vibrational Spectroscopy-Theory and applications", Newage international (p) limited publishers, New Delhi, 2004.

105) Schrader, B. "Infrared and Raman Spectroscopy" VCH Pub., Inc., New York, 1995 195.

106) Scrocco, E.; Tomasi, J. "Electronic Molecular Structure, Reactivity and Intermolecular Forces: An Euristic Interpretation by Means of Electrostatic Molecular Potentials", Adv. Quantum. Chem. 11, 1978, 115-193.

107) Scrocco, E.; Tomasi, J. "The electrostatic molecular potential as a tool for the interpretation of molecular properties", Curr. Chem. 7, 1973, 95-170.

108) Shen, Y.R. “The Principles of Nonlinear Optics”, Wiley, New York, 1984.

109) Silverstein, R.M.; Webster, F.X. “Spectrometric Identification of Organic Compounds”, sixth ed., John Wiley, Asia, 2003.

110) Singh, K.; Kaur, H.; Chibale, K.; Balzarini, J. “Synthesis of 4-aminoquinolinepyrimidine hybrids as potent antimalarials and their mode of action studies”, Eur. J. Med. Chem.66, 2013, 314-323.

111) Socrates, G. “Infrared Characteristic Group Frequencies”, John Wiley and Sons, New York, 1981.

112) Solvia, R.; Luque, F.J.; Orozco, M. “Reliability of MEP and MEP-derived properties computed from DFT methods for molecules containing P, S and Cl”, Theoret. Chem. Accts. 98, 1997, 42-49.

113) Solvia, R.; Orozco, M.; Luque, F.J. “Suitability of density functional methods for calculation of electrostatic properties”, J. Comput. Chem. 18, 1997, 980-991.

114) Souza, M.V.N.; Pais, K.C.; Kaiser, C.R.; Ferreira, M.L.; Lourenço, M.C.S. “Synthesis and in vitro antitubercular activity of a series of quinoline derivatives”, Bioorg. Med. Chem. 17, 2009, 1474-1480.

115) Spalletti, A. “Conformer-specific and two-fold adiabatic photoisomerization of ZZ-1,4-di-(2-quinolylethenyl)benzene,” Photochem. Photobiol. Sci. 3, 2004, 695-699.

116) Spire, A.; Barthes, M.; Kallouai, H.; Nunzio, G.D. “Far-infrared spectra of acetanilide revisited”, Physica D, 137, 2000, 392-406. 196.

117) Sytnik, A.I.; Del Valle, J.C.; “Steady-State and Time-Resolved Study of the ProtonTransfer Fluorescence of 4-Hydroxy-5-azaphenanthrene in Model Solvents and in Complexes with Human Serum Albumin”, J. Phys. Chem. 99, 1995, 13028-13032.

118) Takeuchi, S.; Tahara, T. “Coherent Nuclear Wavepacket Motions in Ultrafast ExcitedState Intramolecular Proton Transfer: Sub-30-fs Resolved Pump-Probe Absorption Spectroscopy of 10-Hydroxybenzo[h]quinoline in Solution”, J. Phys. Chem. A 109, 2005, 10199-10207.

119) Takimoto, C.H.; Wrigth, J.; Arbuck, S.G.; “Clinical applications of the camptothecins”, Biochim. Biophys. Acta. 1400, 1998, 107-119.

120) Tao, Y.T.; Balasubramanian, E.; Danel, A.; Jarosz, B.; P. Tomasik, P. “Sharp green electroluminescence from 1H-pyrazolo[3,4-b]quinoline-based light-emitting diodes,” Appl. Phys. Lett. 77, 2000, 1575-1577.

121) Tokarz, D.; Cisek, R.; Prent, N.; Fekl, U.; Barzda, V. “Measuring the molecular seond hyperpolarizability in absorptive solutions by the third harmonic generation ratio technique,” Analytica Chimica Acta 755 , 86-92, 2012.

122) Trott, O.; Olson, A.J. “AutoDock Vina: Improving the speed and accuracy of docking with a new scoring function, efficient optimization, and multithreading”, J. Comput. Chem. 31, 2010, 455-461.

123) Tsushima, K.; Osumi, T.; Matsuo, N.; Itaya, N.; “Facile Synthesis of Fungicidal NIndanylbenzamide Derivatives: Rearrangement of Tetrahydroquinolines to Aminoindanes”, Agric. Biol.Chem. 53, 1989, 2529-2530.

124) Varsanyi, G. “Assignments of Vibrational Spectra of Seven Hundred Benzene Derivatives”, Wiley, New York, 1974.

125) Wehenkel, A.; Fernandez, P.; Bellinzoni, M.; Catherinot, V.; N. Barilone, N.; G. Labesse, G.; Jackson, M.; Alzari, P.M. “Catalytic domain of protein kinase PknB from Mycobavterium tuberculosis in complex with motoxantrone”, FEBS Lett. 580, 2006, 3018-3022.

126) Wise, R.; Andrews, J.M.; Ashby, J.P.; Matthews, R.S. “In vitro activity of lomefloxacin, a new quinolone antimicrobial agent, in comparison with those of other agents”, Antimicrob.Agents Chemother. 32, 1988, 617-622.

127) Wolinski, K.; Hinton, J. F.; Pulay, P. “Efficient implementation of the gaugeindependent atomic orbital method for NMR chemical shift calculations”, J. Am. Chem. Soc. 112, 1990, 8251-8260.

128) Zhao, J.; Zhang, Y.; Zhu, L. “Theoretical studies on vibrational spectra of mixed cyanide-halide complexes of gold (III)”, J. Mol. Struct. Theochem. 671, 2004, 179- 187.

129) Zhao, Y.; Truhlar, D.G. “Density Functionals with Broad Applicability in Chemistry” Acc. Chem. Res. 41, 2008, 157-167.

130) Zhenming, D.; Heping, S.; Yufang, L.; Diansheng, L.; Bo, L. “Experimental and theoretical study of 10-methoxy-2-phenylbenzo[h]quinoline”, Spectrochim. Acta Part A 78, 2011, 1143-1148.

131) Brown, H.C.,et al., in Baude, E.A. and Nachod, F.C., Determination of Organic Structures by Physical Methods, Academic Press, New York, 1955.