

BISHOP MOORE COLLEGE MAVELIKARA



Project report

on

**SYNTHESIS AND STRUCTURE DETERMINATION OF THE CHALCONE
DERIVATIVE, (2E)-2-(3,4-DIMETHOXYBENZYLIDENE)-3,4-
DIHYDRONAPHTHALEN-1(2H)-ONE: A COMBINED EXPERIMENTAL AND
THEORETICAL APPROACH**

Dissertation submitted to the University of Kerala

In partial fulfilment of the requirement for the award of the Degree of

Bachelor of Science in Physics

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CERTIFICATE

This is to certify that the dissertation entitled “**Synthesis and Structure Determination of the chalcone derivative, (2E)-2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one A Combined Theoretical and Experimental Approach**” by **Sandra Saju S**(Reg. No: 23019101032), **Anusree M S**(Reg. No: 23019101005), **C K Mathew** (Reg. No: 23019101027) and **Vijimol V** (Reg. No: 23019101036) for the award of the degree of Bachelor of Science in Physics is an authentic work under my supervision and guidance during the period 2019 – 2022. Also certified, that the dissertation represents a team work from the part of the candidates.

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Examiners:

1.

2.

DECLARATION OF ORIGINALITY

We, **Sandra Saju S (Reg. No. 23019101032)**, **Anusree M S (Reg. No. 23019101005)**, **C K Mathew (Reg. No. 23019101027)** and **Vijimol V (Reg. No. 23019101036)** hereby declare that this dissertation entitled “**Synthesis and Structure Determination of the chalcone Derivative, (2E)-2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one Chalcone Derivative: A Combined Experimental and Theoretical Approach**” represents our original work carried out as BSc Physics students registered with the University of Kerala and to the best of our knowledge, it contains no material previously published or written by another person, nor any material presented for the award of other degree or Diploma of University of Kerala or any other institution. Any contribution made to this research by others, with whom we have worked at University of Kerala or elsewhere, is explicitly acknowledged in the dissertation. Work of other authors cited in this dissertation have been duly acknowledge under the section “Reference”. We are fully aware that in case of non-compliance detected in future, the Senate of University of Kerala may withdraw the degree awarded to me on the basis of the present dissertation.

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Chapter -1

INTRODUCTION AND THEORETICAL BACKGROUND

Chalcones are a type of flavonoid-like polyphenolic chemicals obtained from plants. They are 1,3-diphenyl-2-propene-1-one, -unsaturated ketones. The term chalcones or chalconoids refers to a group of essential biological substances. Due to their availability in natural products, structural flexibility, biological activities, and high optical nonlinearities that they can exhibit due to large delocalization of the electronic clouds, chalcones and their derivatives have become the material of attraction in recent decades. They also have a wide range of different qualities, which makes them one of the most active research objects in science today. Chalcone is a favoured scaffold in medicinal chemistry since it may be produced in the lab and turned into a variety of heterocyclic scaffolds. It has pharmacological properties and is used in a variety of non-pharmacological applications. Chalcones and their synthetic derivatives have antibacterial, antioxidant, anti-inflammatory, anticancer, anti-histaminic, anti-protozoa, hypnotic, and other major actions, depending on the replacement made on them [1].

The discovery of novel crystals for optical applications, as well as enhanced investigations on the optical properties of materials, has been a growing topic of research. Materials, both organic and inorganic, are thoroughly investigated. Because of their technological usefulness in the areas of optical communication, optical modulators, optical switching, information processing, frequency conversion and doubling, and data storage, crystals with the nonlinear optical response (NLO) are vital in science and modern technology. Usually, organic materials show excellent NLO properties and hence the growth of new organic-based single crystal is important [2].

The chalcone derivatives have attracted significant attention because of their molecular structure and synthetic flexibility that can modify their NLO properties. These properties are reflected by the significant delocalization of π electrons of the chalcone system. The chalcone derivatives with a π conjugated system represent an ideal NLO system, as there is a possibility of large charge transfer through substituent groups on aromatic rings. Strong second harmonic production

in organic systems drives interest in innovative chalcone-based materials in nonlinear optics. Chalcones' high crystallinity adds to their use in second and third order NLO. Thermal stability and good optical limiting behaviour, in addition to these features, are also helpful for its applications. [3, 4]

This study will focus on quantum mechanical analyses of the structure, electrical, and vibrational spectra of an organic chalcone derivative. This research employs computational quantum chemistry, which use a variety of approximation methods, including density functional theory, to get necessary information about the many-electron system under investigation. Computer simulations, which serve as a link between analytic theory and experiment, allowing for the scrutiny of ideas, can also be utilised as an explanatory research tool in physical settings that are not viable in real-world laboratory investigations. As a result, a new multidisciplinary research technique known as Computational Material Science or Computational Physics was born, bringing together aspects from a wide range of disciplines including physics, chemistry, mathematics, biology, engineering, and even medicine. This approach can also be used to perform multiscale and 3multidisciplinary simulations in real-world scenarios. It can be used to figure out a molecule's structure and properties. The information received from experimental results is usually supplemented by computational results. However, in some circumstances, it can anticipate chemical processes that have never been observed before. Structure, absolute and relative (interaction) energies, vibrational frequencies, reactivity, electronic charge density, and other spectroscopic parameters are among the information about the system (molecule/group of molecules/solids) produced by this method.

The fundamental goal of quantum chemical approaches is to acquire approximate solutions to the Schrodinger equation corresponding to the many-electron system, and numerous methods in the realm of quantum physics have been devised and applied in computational programmes to accomplish this. Some of the approaches utilised by such systems include ab initio methods, density-functional methods, and semi-empirical methods. A qualitative or approximate quantitative computational strategy can describe the bulk of chemical phenomena to some extent. To sum up, chalcones are found throughout nature and have been identified as precursors to flavonoids and isoflavonoids. They have a variety of therapeutic effects, including anti-diabetic [3], anti-inflammatory [4], anti-cancer [5], and immunomodulatory [6] properties. The

1,3-diphenyl-2E-propene-1-one chalcone skeleton is made up of a benzylideneacetophenone scaffold with a three-carbon α,β -unsaturated carbonyl bridge connecting the two aromatic structures [7]. Chalcones can be found in nature in a variety of conjugated forms with other moieties. In the synthesis of flavones by aurones, it is an intermediate with an open-chain structure [8]. Several prospective α -glucosidase inhibitors have emerged as a result of the interest in chalcones as anti-diabetic medicines. Yeast α -glucosidase inhibition was observed in new galloyl, caffeoyl, and hexahydroxydiphenyl esters of dihydrochalcone glucosides isolated from the aerial tissues of the *Balanophora tobiracola* plant.

Chalcones are the progenitors to all flavonoids; they have two benzene rings as well as a carbon chain that is structurally similar to propane. In recent years, there has been a major growth in the therapeutic interest in chalcones, as well as their prospective application in cosmetics and the food industry. Antioxidant, antiinflammatory, antiinfective, cytoprotective, hepatoprotective, antiobesity, antidiabetic, anticancer, reversal of multiple drug resistance, antihistamine, antiarrhythmic, platelet antiaggregant, antisteroidal, antiulcer, antiamyloid, antiangiogenic, antinociceptive, anxiolytic, hypnotic, and antispasm are some of the properties of these compounds. In *Z. punctata*, 2',4'-dihydroxychalcone (DHC) and 2', 4'-dihydroxy 3-methoxy chalcone (DHMC) were identified in ethanolic, dichloromethane (DCM), and aqueous (infusion) extracts of aerial parts and flowers. These compounds have known activity as antibacterial, antifungal, antioxidant, and antiinflammatory. In ethanolic and DCM extracts from *Z. punctata* were detected also dihydrochalcones, such as trihydroxydihydrochalcone, 2', 4'-dihydroxydihydrochalcone, and 2', 4'-dihydroxy-3-methoxy dihydrochalcone. Dihydrochalcones have demonstrated a wide range of biological and pharmacological activities, including antioxidant, antiinflammatory, antimicrobial, cytotoxic, and antispasmodic effects. In addition, dihydrochalcones will be reviewed for their well-known use as additives in the food industry. In fact, some dihydrochalcones are known to be intense artificial sweeteners, such as neohesperidin dihydrochalcones obtained by hydrogenation of neohesperidin [9].

1. Theoretical Background

1.1 Quantum Chemical Calculations

Quantum chemical calculations play an ever-increasing role in chemical research and teaching. At first, it was thought that the idea of using mathematics for chemical investigation was irrational. But the introduction of Quantum Mechanics, the fundamental theory that guides the quantum world, changed this notion. Shortly after that, the use of mathematics became common and provided so many methods to extract information about quantum systems. But some problems remained.

Paul A.M Dirac quoted- “The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.” The ultimate aim of every quantum problem is to solve the Schrödinger equation corresponding to the system under study. But it turns out that it is not that simple to solve the equation corresponding to complex systems analytically because of its complexity. So, to solve it, one needs to apply different approximation methods. To get very accurate results, one needs to perform these methods multiple times, which is very difficult and tedious to do by hand. That is where the role of computers comes into play. The advancement in computer technology contributed so much to research fields, especially in physics and chemistry, where computations has so much importance. A good deal of software that makes use of different quantum approximation methods were developed. These are easily available to chemists and physicists, which helped a lot in the research field. The system understudy can be one molecule, a group of molecules, or a solid. Computational chemistry methods involve very approximate and accurate (only for small systems) calculations.

1.1.1 Ab-initio Methods

As said in the previous section, the fundamental aim of quantum chemical methods is to solve the Schrödinger equation and find an approximate solution for the corresponding system. There are several methods that have been implemented to do this. The Ab initio methods are based on theoretical principles and universal physical constants without involving experimental data. These methods are very rigorous mathematical approximations. These methods range from

simplified forms of the first-principles equations that are much easier or faster to solve to approximations limiting the size of the system (for example, periodic boundary conditions), to elementary approximations to the underlying equations that correspond to the system. Some categories of ab-initio methods that are widely used in quantum chemistry and physics are the Hartree-Fock method, Møller- Plesset perturbation theory, configuration interaction, coupled-cluster and reduced density matrices.

Ab initio means ‘from the first principles’ which implies that the only inputs to the ab initio calculations are physical constants. These quantum chemical methods attempt to get approximate solutions to the electronic Schrödinger equation given the positions of the nuclei and the number of electrons in order to yield useful information such as electron densities, energies, and other properties of the system under study.

Other methods are called empirical or semi-empirical because they use additional empirical parameters. These methods use parameters derived from experimental data to simplify computation. Semi-empirical methods are often applied to large systems. These methods are relatively inexpensive and can provide a reasonably qualitative description of molecular systems and fairly accurate quantitative predictions of energies and structures for systems where good parameter sets exist. Ab initio methods, in contrast, use no experimental parameters; instead, their computations are based completely on the fundamental laws of quantum mechanics. They are able to provide high-quality quantitative predictions for a wide range of systems and are not limited to any specific class or size of a system.

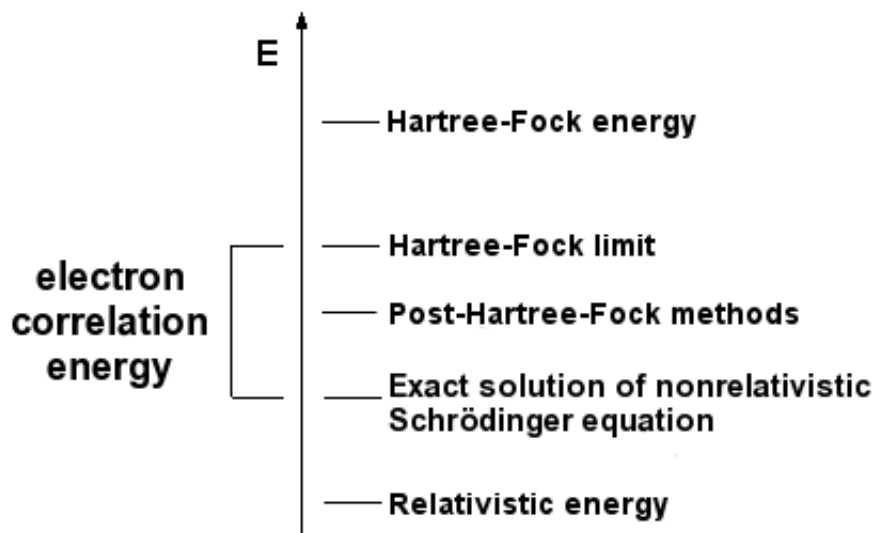


Fig 1.2 Diagram illustrating various *ab initio* electronic structure methods in terms of energy.

1.1.2 Density Functional Theory

Density functional theory is one of the quantum mechanical theories that is actively used in chemistry and physics due to its capability to treat electron correlation with low computational cost as compared to correlated *ab-initio* post-HF methods. The accuracy and efficiency offered by the DFT method is especially important for large systems. DFT methods compute electron correlation via general functionals of the electron density.

Hohenberg–Kohn theorems

The foundation of density functional theory rests on two fundamental theorems proved by Kohn and Hohenberg and a set of equations formulated by Kohn and Sham. Hohenberg–Kohn theorems apply to any system consisting of electrons moving under the influence of an external potential.

Theorem 1. The external potential (and hence the total energy), is a unique functional of the electron density.

This theorem states that there exists a one-to-one mapping between the ground-state wave function and the ground-state electron density. So according Hohenberg and Kohn the ground-state energy E can be expressed as $E[n(\mathbf{r})]$ (functional of electron density), where $n(\mathbf{r})$ is the

electron density. This is why this field is known as density functional theory. In other words, Hohenberg and Kohn's result can be restated as: the ground-state electron density uniquely determines all properties, including the energy and wave function, of the ground state.

Theorem 2. The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.

If we know the appropriate functional form, then we could vary the electron density until the energy from the functional is minimized, which will give some information for finding the relevant electron density. This variational principle is used in practice with approximate forms of the functional [10].

1.1.3 Gaussian Program Package

Gaussian'09 could be a framework of program that performs semi empirical and *ab initio* atomic calculations.

Gaussian is able of anticipating numerous properties such as [11].

- Multiple moments
- Molecular orbital
- Reaction pathways
- Bond and reaction energies
- Thermo chemical properties
- IR and Raman spectra
- Vibrational frequencies
- Energy and structure of transition states
- Molecular energies and structures
- Vibrational circular dichorism intensities
- NMR shielding and magnetic susceptibilities

1.1.4 Z-matrix

The Z-matrix provides a description of each atom in a molecule in terms of the internal coordinates.

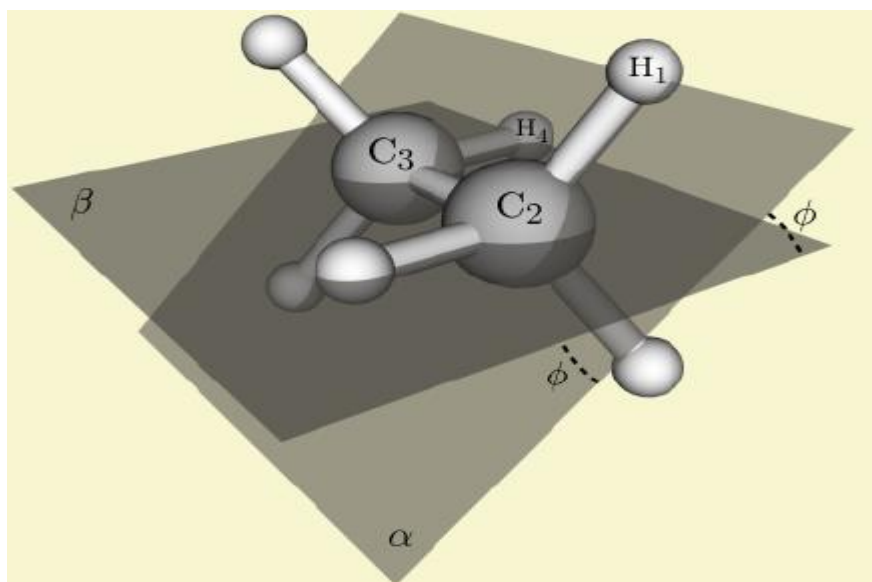
Internal coordinates:

- Species of each atom
- Distances
- Angles
- Torsion (dihedral) angles

This is particularly useful when working with molecular systems or restricted optimizations (control optimization variables). The name arises because the Z-matrix assigns the second atom along the Z-axis from the first atom, which is at the origin.

When constructing a Z-matrix, must follow these steps:

1. Draw the molecule.
2. Assign one atom to be #1.
3. Starting with atom #1, assign all other atoms a sequential number. List the atoms you numbered, in order, one right under the other.
4. Place the atom designated as #1 at the origin of coordinate system. The first atom does not have any defining measurements since it is at the origin.
5. To identify the second atom, define its bond length to the first atom.
6. For the third atom, define a bond length to atom #1 and a bond angle between atom #3 and atoms #1 and #2. (Bond angles are the angles between three atoms.)
7. Remember that, only use previously defined atoms when defining the current atom. This means that it can not be the reference atom #7 when defining atom #5.
8. To identify atom #4 and all other atoms, must include a bond length, bond angle and a dihedral angle. (Dihedral angles are the angles between an atom and the plane created by three other atoms.) This is done by using neighboring atoms to the atom which are describing.



1.1.5 Basis Set

The molecular orbital in a molecule can be represented with the aid of the assist of the foundation set and the interpretation of the basis set can be achieved via confining each and every electron to a specific vicinity of space. The aircraft wave basis functions helps in necessitating the use of a pseudo-potential that helps in the representation of the atomic core electrons/potential. For periodic systems, nuclear centered groundwork features can also be used and this treats all electrons are handled on an equal footing. In recent traits finite-element techniques are used the place piecewise polynomials are used for representing the orbital's [12-14]. The wave function is represented as a vector in the foundation set and the elements of this foundation set corresponds to coefficients of the basis features in the linear enlargement [15]. The specific sort of foundation sets are represented in accordance with their increased size.

1.1.6 Minimal Basis Set

Negligible premise sets is the littlest premise set. A single premise work is utilized for each orbital in a Hartree-fock calculation on the free molecule, on each iota within the particle in a negligible premise set [12]. Commonly utilized negligible premise sets of this sort are;

- STO-3G
- STO-4G
- STO-6G
- STO-3G*-Polarized adaptation of STO-3G[12,16]

1.1.7 Split Valence Basis Set

Valance electrons are the ones that are dependable for the holding interaction. This basis set is additionally known as pople premise set. Here could be a list of commonly utilized split-valance premise set. Here could be a list of commonly utilized split valance premise sets of this sort [17, 18].

- 3-21G
- 3-21G* - Polarization functions on heavy atoms
- 3-21G** - Polarization functions on heavy atoms and hydrogen
- 3-21+G - Diffuse functions on heavy atoms
- 3-21++G - Diffuse functions on heavy atoms and hydrogen

- 3-21+G* - Polarization and diffuse functions on heavy atoms
- 3-21+G** - Polarization functions on heavy atoms and hydrogen, as well as diffuse functions on heavy atoms.
- 4-21G
- 4-31G
- 6-21G
- 6-31G
- 6-31G*
- 6-31+G*
- 6-31G(3df, 3pd)
- 6-311G
- 6-311G*
- 6-311+G*

1.1.8 Completeness-optimized Basis Set

Manninen and varra [19] proposed completeness optimized groundwork sets. The place the exponents are acquired by using maximization of one-electron completeness profile [20]. Alternatively of minimization of the energy completeness-optimized foundation sets are without problems approach basis set restrict of any property at any stage of principle for the completeness, and the mechanism is additionally comparatively less difficult to operate [21].

1.2 X-Ray Diffraction (XRD) as a tool for Structure Determination

In material science, XRD is a non-destructive technique for determining the crystallographic structure of a substance. XRD works by irradiating a material with incident x-rays and then measuring the intensities and scattering angles of the x-rays that escape. Max Van Laue observed in 1912 that the crystalline substance acts as a three-dimensional diffraction grating for X-ray wavelengths with plane spacing similar to that of a crystal lattice. The identification of materials based on their diffraction patterns, as well as phase identification, are two of the most common

applications of XRD analysis. It also reveals how the actual structure differs from the ideal one as a result of internal stress and flaws.

X-rays are waves of electromagnetic energy, whereas crystals are regular arrays of atoms. When an X-ray beam strikes the atoms or molecules of a crystal lattice, the incident X-rays are elastically scattered by electrons around the atoms or molecules. The scattered waves cancel each other out in the majority of directions due to destructive interference. The scattered X-rays interfere constructively at particular values of the incident angle (or along specific directions) of the X-ray beam, resulting in diffraction patterns.

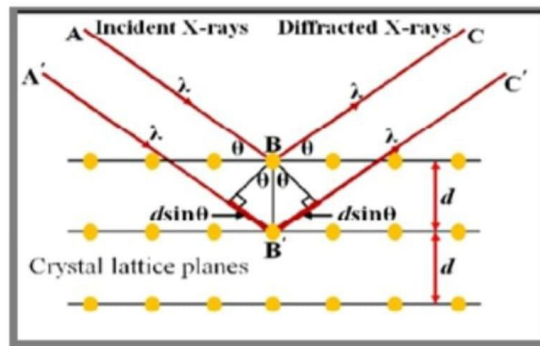


Figure 3.1 Illustration of Bragg's Law

Bragg's law is what determines this angle. According to Bragg's law, the scattered X-ray beams will interfere constructively and produce diffraction patterns when the path difference between the beams is an integral multiple of the wavelength of the X-ray, which is given by

$$2d\sin\theta = n\lambda$$

where 'n' is the diffraction order, 0.15418nm is the X-ray wavelength, 'd' is the crystal's interplanar spacing, and is the Bragg's angle [9].

X-ray diffractometer

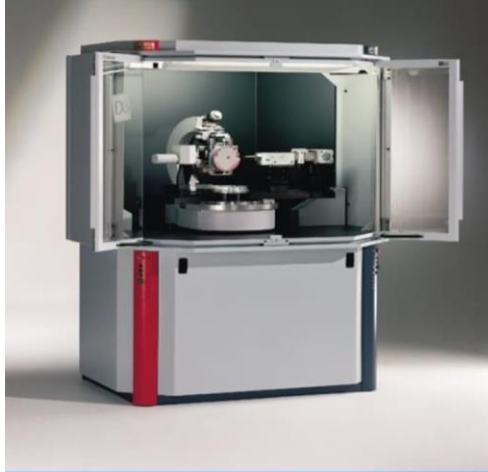


Figure 3.2 X-ray diffractometer

An X-ray tube, a sample holder, and an X-ray detector are the three fundamental components of an X-ray diffractometer. In a cathode ray tube, X-rays are produced by heating the tube to produce electrons and then accelerating the electrons towards a target material with electrons. The typical X-ray spectra are created when electrons have enough energy to push out the inner shell electron. The X-rays are collimated and focused on the sample. The intensity of the reflected X-ray is recorded when the sample detectors spin. When Bragg's law is met, diffracted beams interfere constructively, resulting in diffraction peaks. A detector captures this signal, analyses it, and converts it to a count rate, which is subsequently sent to a device like a computer monitor.

An X-ray diffract meter's shape is such that the sample rotates at an angle of 2θ in the direction of the collimate X-ray beam. Due to the random orientation of the powdered material, scanning the sample through a range of 2θ angles should yield all potential lattice diffraction directions. Because each mineral has its own set of d-spacing, converting the diffraction peaks to interplanar spacing or d-spacing allows for mineral identification. The resultant d-spacing is compared to conventional reference patterns to achieve this. Information about the structural physical properties can be derived from XRD data. In completely crystalline samples, the diffraction peaks are sharp. For polycrystalline materials, broad peaks are obtained.

To calculate the crystallite size, Scherrere's equation is used, which is given as:

$$D = K\lambda / (\beta \cos\theta)$$

Where D is the crystallite size, K is the form factor, K=0.9, 0.15418nm is the X-ray wavelength, β is the entire width at half maximum, and θ is the Bragg angle.

Chapter-2

LITERATURE REVIEW

C.shuruthi *et.al* studied a nonlinear optical active Thineyl chalcone ($C_{16}H_{15}ClO_4S$) were characterized using various experimental techniques. The theoretical investigations was also carried out. The obtained GCRD parameters such as I, A, χ , η , σ , ω , μ denotes excellent chemical strength and kinetic stability. Which suggest the stability of the material for optoelectronic applications [22].

Recently, two halogenated chalcone derivatives containing Thiophene moiety are found to be typical prospective candidates for optical devices on account of their unique and remarkable NLO properties. Vasant s.Naik *et.al* did a structural, linear optical, second and third-order nonlinear optical studies of two halogenated chalcone derivatives containing Thiophene moiety. NLO property of B3B2SC and C3B2SC were examined using Quantum chemical computations at B3LYP/6-31+G theory. Their study concluded that, both the crystals had high thermal stability, higher second and third-order nonlinear optical properties and high polarization. So these chalcone derivatives are highly recommended for optical devices [23].

Two non-centrosymmetric thiophene-chalcone derivatives are found and can be used in optical devices as frequency generator, optical switch and optical limiter by evaluating the chalcones namely, (2E)-1-(5-bromothiophen-2-yl)-3-(3-fluorophenyl) prop-2-en-1-one (3F5B2SC) and (2E)- 1-(5-bromothiophen-2-yl)-3-(4-methoxyphenyl) prop-2-en-1-one (4M5B2SC) by structural, linear optical, thermal and nonlinear optical studies. The enhanced SHG and THG efficiency of these chalcones showed that it can be used for frequency doubling and other NLO applications [24].

Jean M F Custodio *et.al* did synthesis, structural and optical properties of benzene-sulfonyl incorporated chalcones. The study was essentially seeking for the NLO response double functionalized compound. The study that incorporation of benzene sulfonyl to the main structure of chalcone which does not have much influence on NLO properties [25].

H. Belahlou et al. synthesized, performed structural analysis and studied nonlinear optical (NLO) properties of four novel organo electronics chalcone derivatives : [1: (E)-2-(1-(3-oxo-1,3-diphenylprop-1-en-2-yl)pyridin-2(1H)-ylidene)malononitrile, 2 : (E) – 2 - (1 - (3- oxo – 3 - phenyl-1-(p-tolyl)prop-1-en-2-yl)pyridin-2(1H)-ylidene)malononitrile, 3 : (E) - 2 - (1 - (1 - (4 - methoxyphenyl) - 3- oxo – 3 - phenylprop-1-en-2-yl)pyridine – 2 (1 H) -ylidene) malononitrile, 4: (E) – 2 - (1 - (1 - (4 – chlorophenyl) – 3 – oxo – 3 - phenylprop-1-en-2- yl)pyridin-2(1H)ylidene)malononitrile]. Structural characterization was done using single-crystal X-ray diffraction, 1H and ^{13}C NMR, FTIR and UV–Visible spectral analysis. Third harmonic generation (THG) measurements have been performed on thin films at 1064 nm. Induced second harmonic generation measurements are also performed. The highest response of both, SHG and THG was observed for compound 1. This behaviour may be explained by the molecular structure of 1 and more efficient charge transfer generated by a favourable three-dimensional intermolecular interactions network. They concluded that compound 1 is a better NLO candidate [26].

A dual approach study will always good because it will give better understanding of the work and a comparison study is possible. A dual approach study on (E)-1-(4-Bromophenyl)-3-(2-chlorophenyl) prop-2-en-1-one(1), (E)-3-(3-Bromophenyl)-1-(4-methoxyphenyl) prop-2-en-1-one (2) and (E)-3-(4-Chlorophenyl)-1-(2-furyl) prop-2-en-1-one (3) chalcone derivatives reported by Mohd. Shkir et.al UV–vis-NIR, X-ray diffraction and Photoluminescence spectroscopy techniques in experimental part and also quantum chemical density functional theory calculations were executed to get the linear optical, second and third-order nonlinear optical (NLO) properties as well as transfer integrals of all three systems. The experimental and theoretically calculated properties are found to be in great agreement with each other. They found that these chalcone derivatives are excellent choice for semiconductor devices due to the excellent intra- and inter-molecular charge transport from occupied to unoccupied molecular orbitals. The compound (3) is found to have way better NLO activities and thermal steadiness compared to (1) and (2). Bigger electron exchange necessarily values than hole ones uncovered that examined compounds would be superior electron transport materials and can function as n-type in organic semiconductor devices [27].

Chalcones has biological activities such as ulcer, cancer, HIV, and malaria prevention, acts as a fungicide and antioxidant, and is both anti-inflammatory and anti-mitotic and also have applications in in biological chemistry. These days, quantum chemical calculations have been demonstrated to be an imperative tool for examination of the relationship between structures and spectral properties of the organic molecules and for the elucidation of experimental information emerging from industrial interest and applications. Yunsheng Xue et.al investigated the structures and spectral properties of substituted chalcones using DFT and TD-DFT. The quantum mechanical computation reported that good evidence of the intramolecular charge transference of the HOMO→LUMO transitions for the 4'-NO₂ molecule and the maximum absorption band mainly results from the $\pi\rightarrow\pi^*$ transition from the HOMO to the LUMO [28].

Chapter-3

RESULT AND DISCUSSION

3.1 Synthesis of (2E)-2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one: Claisen – Schmidt condensation

Equimolar quantities of 3,4- dimethoxy benzaldehyde (2.51 g, 0.015 mol) and -tetralone(2.0 ml, 0.015 mol) were dissolved in ethanol in a 250 ml conical flask and stirred for 15 min. Freshly prepared 10% NaOH solution was added to the mixture and stirred again for 1 h. This mixture was kept at room temperature for 24 h and then poured into ice-cold water. A yellow precipitate formed, which was washed with distilled water to remove any traces of NaOH. The filtered, dried crude product was recrystallized three times from acetone solution. After four days, yellow blocks of were harvested.

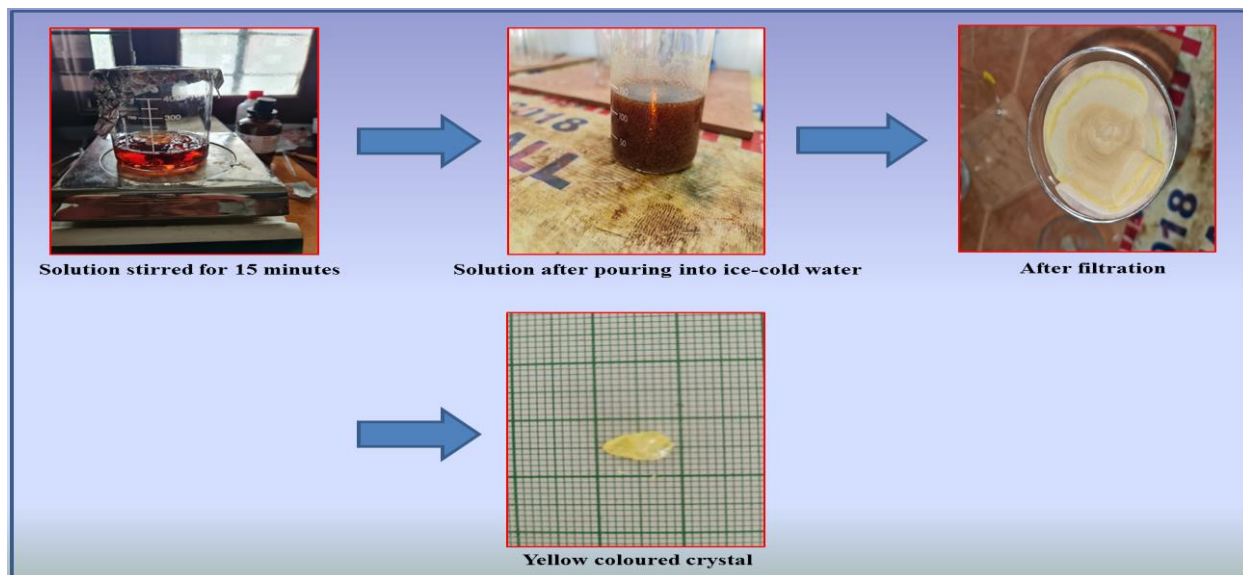


Figure 3.1 synthesis of (2E)-2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one

3.2 Crystal structure from Single Crystal XRD

The single crystal X ray diffraction analysis has been deployed to understand the interactions. The structure has been published in Cambridge Crystallographic Data Centre with DOI10.5517/ccdc.csd.cc242lkd and CCDC number 1968703, from where the parameters are accessible in CIF format. It has been confirmed that (2E)-2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one belongs to the Orthorhombic crystal system in the $P2_12_12_1$ space group with cell parameters $a=7.8906(7)$ Å, $b=9.4104(8)$ Å and $c=20.7764(19)$ Å, $\alpha=90^\circ$, $\beta=90^\circ$ and $\gamma=90^\circ$ in tune with its reported structure [29]. The structure was solved by direct method procedures as implemented in SHELXS2008 program.

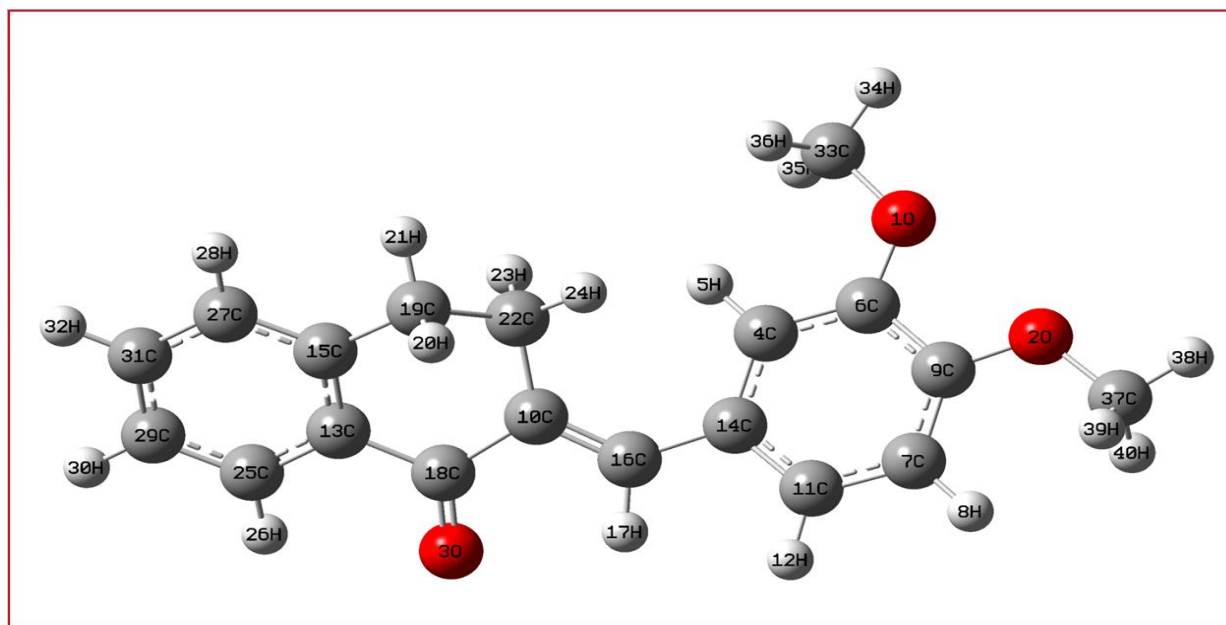
Table 3.1 Crystallographic data and structure refinement for (2E)-2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one)

Empirical Formula	C ₁₉ H ₁₈ O ₃
Formula Weight	294.33
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal System	orthorhombic
Space Group	P2 ₁ 2 ₁ 2 ₁
Unit Cell Dimensions	a = 7.8906(7) Å $\alpha = 90^\circ$ b = 9.4104(8) Å $\beta = 90^\circ$ c = 20.7764(19) Å $\gamma = 90^\circ$
Z	4
Volume	1542.7(2) Å ³
Density	1.267 g/cm ³
Absorption coefficient	0.085 mm ⁻¹
F (000)	624
Crystal Size	0.350 x 0.400 x 0.450 mm
Theta range for data collection	2.92 to 28.46°
Index ranges	-10<=h<=10, -11<=k<=11, -27<=l<=27
Reflections collected	17019
Independent reflections	3824 [R(int) = 0.0503]
Refinement method	Full-matrix least-squares on F ²
Data/Restraints/Parameters	3824 / 0 / 202
Goodness-of-fit on F ²	1.037
Final R indices [I > 2sigma(I)]	R1 = 0.0413

	wR2 = 0.0956
R indices (all data)	R1 = 0.0531
	wR2 = 0.1029
Largest diff. peak and hole	0.168 and -0.164 eÅ ⁻³

Optimized Geometry from Gaussian '09 program

The quantum chemical computations on (2E)-2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one, C₁₉H₁₈O₃ were carried out using the Gaussian 09W program package at the B3LYP Density Functional Theory method with 6-31++g(d,p) basis set[13]. The optimized geometrical parameters of (2E)-2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one have been calculated by using B3LYP functional with 6-31++g(d,p) basis set. The parameters obtained from the computation are found to be comparable with the XRD data as understood from the parameters listed in table 3.1 and the optimized structure is shown in Fig. 3.1.



Optimized Geometry of (2E)-2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one at the B3LYP/6-31++g(d,p) level

Table 3.2 Input molecule specification of (2E)-2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one at B3LYP/6-31++g(d,p) level.

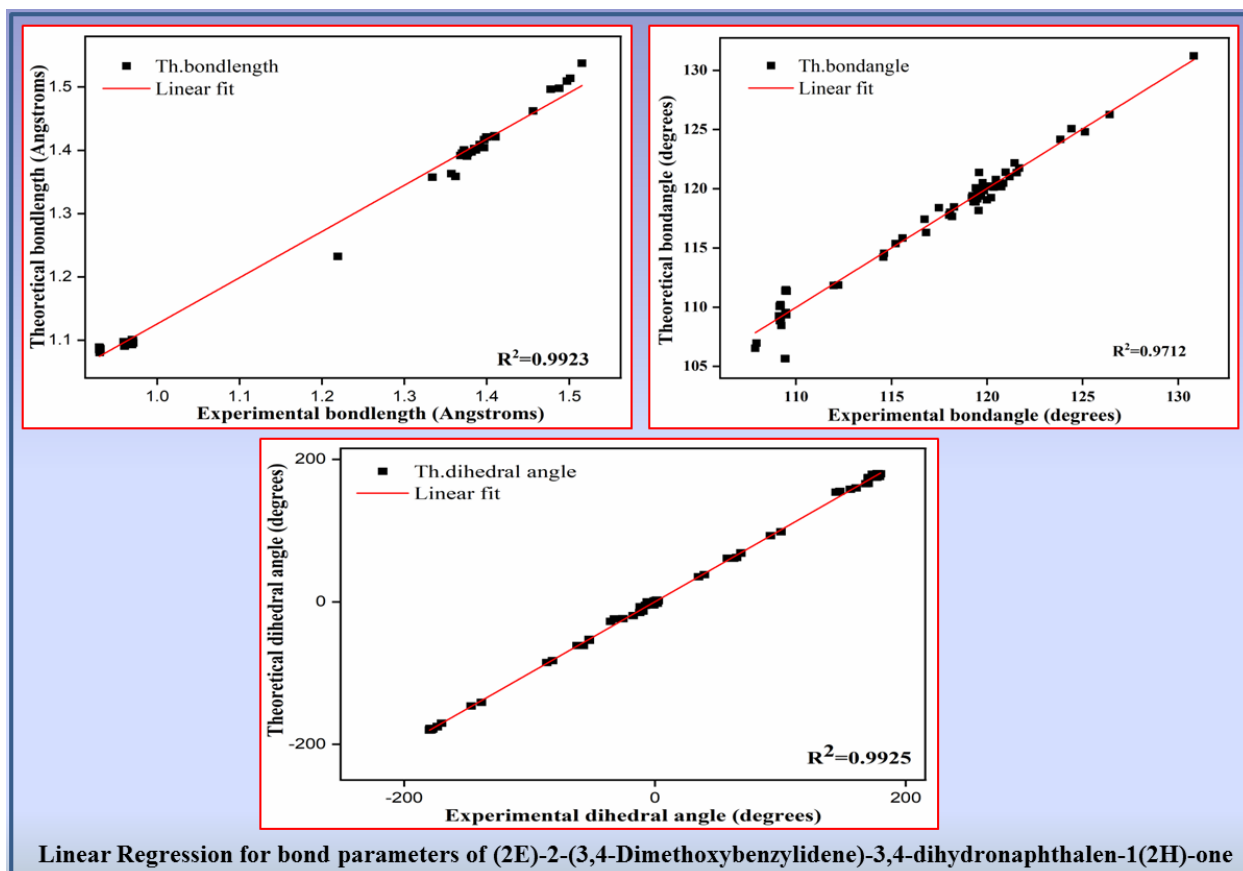
O	3.85358000	1.91996600	-0.54884700
O	5.48957300	0.07316700	0.22704600
O	-2.44077300	-2.38873900	-0.68826500
C	1.92682600	0.43095800	-0.37842800
H	1.25508100	1.19740100	-0.73717200
C	3.28255500	0.71431700	-0.27161200
C	3.69500200	-1.57636400	0.41479100
H	4.37114300	-2.36639000	0.71817400
C	4.18604000	-0.29991700	0.14411500
C	-1.12143800	-0.48565100	-0.09031600
C	2.33293900	-1.85222600	0.28716500
H	1.97252000	-2.85525400	0.49423100
C	-3.68176700	-0.45869800	-0.10940800
C	1.41829400	-0.85775600	-0.08490600
C	-3.69406500	0.77156700	0.57435400
C	0.00907700	-1.22749400	-0.18742600
H	-0.17187900	-2.28849000	-0.35380100
C	-2.40903700	-1.21556400	-0.31941000
C	-2.40337400	1.31660100	1.13548100
H	-2.22885800	0.88158900	2.12980600
H	-2.48136800	2.39940000	1.28116300
C	-1.20147700	0.99023100	0.23397100
H	-1.29364100	1.57537200	-0.69364800
H	-0.28312300	1.31984600	0.72629200
C	-4.87858800	-1.00668400	-0.59350800
H	-4.82989500	-1.96261900	-1.10410900
C	-4.91238400	1.43662000	0.74630400
H	-4.93088600	2.38844400	1.27134300
C	-6.08285100	-0.33496500	-0.41773900
H	-7.00646900	-0.75920800	-0.79999600
C	-6.09755100	0.89218100	0.25310000
H	-7.03382900	1.42592500	0.39029500
C	3.00964600	2.97565500	-0.97676100
H	3.66174200	3.83685100	-1.12827500
H	2.50450100	2.73516200	-1.92119400
H	2.25396900	3.22346900	-0.21993000
C	6.44052100	-0.90506000	0.61873000
H	7.40667000	-0.39908100	0.61741500
H	6.23444400	-1.28917000	1.62582800
H	6.47062300	-1.74489900	-0.08687900

Table 3.3 Optimized geometric parameters of (2E)-2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one

Parameter	Bond Lengths (Å)		Parameter	Bond Angles (°)		Parameter	Dihedral Angles (°)	
	631++G (d,p)	X-ray		631++G (d,p)	X-ray		631++G (d,p)	X-ray
O1-C6	1.3631	1.35708	C6-O1-C33	118.4632	118.26	C33-O1-C6-C4	-0.3222	1.2978
O1-C33	1.4211	1.41045	C9-O2-C37	118.4081	117.48	C33-O1-C6-C9	179.2234	-178.41
O2-C9	1.3587	1.36193	H5-C4-C6	119.1568	119.48	C6-O1-C33-H34	179.8381	177.85
O2-C37	1.4227	1.40923	H5-C4-C14	119.3842	119.53	C6-O1-C33-H35	-61.4604	-62.18
O3-C18	1.2324	1.21897	C6-C4-C14	121.3946	120.97	C6-O1-C33-H36	61.1611	57.82
C4-H5	1.0806	0.93019	O1-C6-C4	124.807	125.12	C37-O2-C9-C6	-179.038	173.55
C4-C6	1.3907	1.37582	O1-C6-C9	115.3564	115.21	C37-O2-C9-C7	0.0305	-6.19
C4-C14	1.4169	1.39672	C4-C6-C9	119.8351	119.64	C9-O2-C37-H38	179.9148	-177.22
C6-C9	1.421	1.39949	H8-C7-C9	120.2281	120.01	C9-O2-C37-H39	-61.3738	-57.192
C7-H8	1.0833	0.93016	H8-C7-C11	119.2575	120.21	C9-O2-C37-H40	61.2005	62.83
C7-C9	1.3955	1.36995	C9-C7-C11	120.5116	119.77	H5-C4-C6-O1	1.9816	0.9017
C7-C11	1.3973	1.38162	O2-C9-C6	115.8376	115.58	H5-C4-C6-C9	-177.545	-179.39
C10-C16	1.3575	1.33387	O2-C9-C7	125.08	124.42	C14-C4-C6-O1	179.0444	-179.07
C10-C18	1.4979	1.48785	C6-C9-C7	119.0761	119.99	C14-C4-C6-C9	-0.4823	0.6291
C10-C22	1.5137	1.50105	C16-C10-C18	116.3025	116.81	H5-C4-C14-C11	175.7247	178.99
C11-H21	1.0859	0.93019	C16-C10-C22	126.256	126.41	H5-C4-C14-C16	-2.0107	1.907
C11-C14	1.4026	1.38473	C18-C10-C22	117.4362	116.73	C6-C4-C14-C11	-1.3315	-1.027
C13-C15	1.4089	1.39151	C7-C11-H12	119.2359	119.2	C6-C4-C14-C16	-179.067	-178.11
C13-C18	1.4963	1.47741	C7-C11-C14	121.3554	121.56	O1-C6-C9-O2	0.9039	-0.605
C13-C25	1.4044	1.39648	H12-C11-C14	119.4046	119.23	O1-C6-C9-C7	-178.224	179.151
C14-C16	1.4622	1.45608	C15-C13-C18	121.0342	121.18	C4-C6-C9-O2	-179.526	179.66
C15-C19	1.5093	1.49738	C15-C13-C25	120.0674	119.41	C4-C6-C9-C7	1.3458	-0.58
C15-C27	1.4004	1.38667	C18-C13-C25	118.8933	119.39	H8-C7-C9-O2	-0.0205	0.626
C16-H17	1.0891	0.9296	C4-C14-C11	117.7848	118.02	H8-C7-C9-C6	179.0204	-179.1
C19-H20	1.0997	0.97045	C4-C14-C16	124.1694	123.84	C11-C7-C9-O2	-179.412	-179.31
C19-H21	1.0956	0.97068	C11-C14-C16	118.0087	118.06	C11-C7-C9-C6	-0.3714	0.9484
C19-C22	1.5374	1.51548	C13-C15-C19	119.3202	119.29	H8-C7-C11-H12	-0.1632	-1.287
C22-H23	1.101	0.96939	C13-C15-C27	118.9082	119.29	H8-C7-C11-C14	179.0949	178.66
C22-H24	1.093	0.96953	C19-C15-C27	121.7526	121.68	C9-C7-C11-H12	179.2344	178.65
C25-H26	1.0851	0.92972	C10-C16-C14	131.2211	130.81	C9-C7-C11-C14	-1.5075	-1.392
C25-C29	1.3918	1.36805	C10-C16-H17	114.2267	114.57	C18-C10-C16-C14	176.8233	179.08
C27-H28	1.0873	0.93034	C14-C16-H17	114.544	114.6	C18-C10-C16-H17	-4.2945	-0.954
C27-C31	1.3959	1.37707	O3-C18-C10	122.1806	121.44	C22-C10-C16-C14	-4.0374	-3.05

C ₂₉ -H ₃₀	1.086	0.93087	O ₃ -C ₁₈ -C ₁₃	120.1461	120.35	C ₂₂ -C ₁₀ -C ₁₆ -H ₁₇	174.8447	176.9
C ₂₉ -C ₃₁	1.4004	1.37226	C ₁₀ -C ₁₈ -C ₁₃	117.6643	118.16	C ₁₆ -C ₁₀ -C ₁₈ -O ₃	-6.7211	-11.8
C ₃₁ -H ₃₂	1.0865	0.93039	C ₁₅ -C ₁₉ -H ₂₀	109.2653	109.11	C ₁₆ -C ₁₀ -C ₁₈ -C ₁₃	174.3694	170.43
C ₃₃ -H ₃₄	1.0906	0.96046	C ₁₅ -C ₁₉ -H ₂₁	110.1118	109.2	C ₂₂ -C ₁₀ -C ₁₈ -O ₃	174.061	170.12
C ₃₃ -H ₃₅	1.0974	0.95931	C ₁₅ -C ₁₉ -C ₂₂	111.8659	112.21	C ₂₂ -C ₁₀ -C ₁₈ -C ₁₃	-4.8486	-7.6414
C ₃₃ -H ₃₆	1.0976	0.95961	H ₂₀ -C ₁₉ -H ₂₁	106.5228	107.87	C ₁₆ -C ₁₀ -C ₂₂ -C ₁₉	-140.96	-138.39
C ₃₇ -H ₃₈	1.0905	0.96029	H ₂₀ -C ₁₉ -C ₂₂	108.8559	109.16	C ₁₆ -C ₁₀ -C ₂₂ -H ₂₃	98.3836	100.49
C ₃₇ -H ₃₉	1.0971	0.95966	H ₂₁ -C ₁₉ -C ₂₂	110.0626	109.15	C ₁₆ -C ₁₀ -C ₂₂ -H ₂₄	-19.3977	-17.31
C ₃₇ -H ₄₀	1.0971	0.95986	C ₁₀ -C ₂₂ -C ₁₉	111.8326	111.97	C ₁₈ -C ₁₀ -C ₂₂ -C ₁₉	38.1708	39.46
			C ₁₀ -C ₂₂ -H ₂₃	110.1108	109.17	C ₁₈ -C ₁₀ -C ₂₂ -H ₂₃	-82.4858	-81.64
			C ₁₀ -C ₂₂ -H ₂₄	110.2164	109.19	C ₁₈ -C ₁₀ -C ₂₂ -H ₂₄	159.7329	160.55
			C ₁₉ -C ₂₂ -H ₂₃	108.4568	109.24	C ₇ -C ₁₁ -C ₁₄ -C ₄	2.3292	1.40982
			C ₁₉ -C ₂₂ -H ₂₄	109.113	109.21	C ₇ -C ₁₁ -C ₁₄ -C ₁₆	-179.793	178.66
			H ₂₃ -C ₂₂ -H ₂₄	106.9716	107.94	H ₁₂ -C ₁₁ -C ₁₄ -C ₄	-178.414	-178.63
			C ₁₃ -C ₂₅ -H ₂₆	118.1599	119.55	H ₁₂ -C ₁₁ -C ₁₄ -C ₁₆	-0.5361	-1.378
			C ₁₃ -C ₂₅ -C ₂₉	120.4692	120.85	C ₁₈ -C ₁₃ -C ₁₅ -C ₁₉	-1.1894	-2.2575
			H ₂₆ -C ₂₅ -C ₂₉	121.3709	119.58	C ₁₈ -C ₁₃ -C ₁₅ -C ₂₇	-179.632	179.22
			C ₁₅ -C ₂₇ -H ₂₈	119.3838	119.68	C ₂₅ -C ₁₃ -C ₁₅ -C ₁₉	177.9771	177.21
			C ₁₅ -C ₂₇ -C ₃₁	120.7708	120.46	C ₂₅ -C ₁₃ -C ₁₅ -C ₂₇	-0.4653	-1.295
			H ₂₈ -C ₂₇ -C ₃₁	119.8454	119.85	C ₁₅ -C ₁₃ -C ₁₈ -O ₃	166.0576	170.06
			C ₂₅ -C ₂₉ -H ₃₀	120.1979	120.24	C ₁₅ -C ₁₃ -C ₁₈ -C ₁₀	-15.0097	-12.146
			C ₂₅ -C ₂₉ -C ₃₁	119.611	119.49	C ₂₅ -C ₁₃ -C ₁₈ -O ₃	-13.1185	-9.41
			H ₃₀ -C ₂₉ -C ₃₁	120.191	120.26	C ₂₅ -C ₁₃ -C ₁₈ -C ₁₀	165.8142	168.37
			C ₂₇ -C ₃₁ -C ₂₉	120.1706	120.75	C ₁₅ -C ₁₃ -C ₂₅ -H ₂₆	-179.442	-179.21
			C ₂₇ -C ₃₁ -H ₃₂	119.7646	119.6	C ₁₅ -C ₁₃ -C ₂₅ -C ₂₉	0.6091	0.83
			C ₂₉ -C ₃₁ -H ₃₂	120.0646	119.63	C ₁₈ -C ₁₃ -C ₂₅ -H ₂₆	-0.2575	0.2725
			O ₁ -C ₃₃ -H ₃₄	105.6621	109.42	C ₁₈ -C ₁₃ -C ₂₅ -C ₂₉	179.7933	-179.68
			O ₁ -C ₃₃ -H ₃₅	111.4702	109.46	C ₄ -C ₁₄ -C ₁₆ -C ₁₀	-27.3305	-35.42
			O ₁ -C ₃₃ -H ₃₆	111.4485	109.49	C ₄ -C ₁₄ -C ₁₆ -H ₁₇	153.7901	144.61
			H ₃₄ -C ₃₃ -H ₃₅	109.3608	109.5	C ₁₁ -C ₁₄ -C ₁₆ -C ₁₀	154.9388	147.48
			H ₃₄ -C ₃₃ -H ₃₆	109.35	109.46	C ₁₁ -C ₁₄ -C ₁₆ -H ₁₇	-23.9406	-32.47
			H ₃₅ -C ₃₃ -H ₃₆	109.4568	109.46	C ₁₃ -C ₁₅ -C ₁₉ -H ₂₀	-85.3386	-86.29
			O ₂ -C ₃₇ -H ₃₈	105.6399	109.45	C ₁₃ -C ₁₅ -C ₁₉ -H ₂₁	157.9936	156
			O ₂ -C ₃₇ -H ₃₉	111.3651	109.44	C ₁₃ -C ₁₅ -C ₁₉ -C ₂₂	35.2696	34.83
			O ₂ -C ₃₇ -H ₄₀	111.3432	109.52	C ₂₇ -C ₁₅ -C ₁₉ -H ₂₀	93.0579	92.17
			H ₃₈ -C ₃₇ -H ₃₉	109.4269	109.48	C ₂₇ -C ₁₅ -C ₁₉ -H ₂₁	-23.6099	-25.51
			H ₃₈ -C ₃₇ -H ₄₀	109.4391	109.44	C ₂₇ -C ₁₅ -C ₁₉ -C ₂₂	-146.334	-146.69
			H ₃₉ -C ₃₇ -H ₄₀	109.5369	109.47	C ₁₃ -C ₁₅ -C ₂₇ -H ₂₈	-179.936	-178.75
						C ₁₃ -C ₁₅ -C ₂₇ -C ₃₁	0.0382	1.194
						C ₁₉ -C ₁₅ -C ₂₇ -H ₂₈	1.6615	2.764

From Table 3.3, it can be seen that there are some deviations in the computed geometric parameters from those obtained from XRD data and these differences are probably due to the intermolecular interactions in the crystalline state. The strong repulsion between H₂₃ and H₂₄ leads to the enlargement of angles C₁₀-C₁₆-C₁₄ and C₂₂-C₁₀-C₁₆ by 11° and 6°, respectively from 120°. The shortening of angles C₆-O₁-C₃₃ and C₉-O₂-C₃₇ is the consequence of the sharing of lone pair electrons of the methyl group with the p electrons in the ring and the interaction of these lone pair electrons with the nearby π system. Due to the charge delocalization, the calculated C-C bond lengths (~1.40 Å) are differing from that of standard values (1.54 Å). The parameters obtained from the computation are found to be comparable with the XRD data as understood from the linear regression analysis shown in Fig.3.2, with R² values of 0.9923, 0.9712 and 0.9925 for the fit of bond lengths, bond angles and dihedral angles respectively.



Chapter-4

CONCLUSION

The organic NLO crystal (2E)-2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one has been synthesized according to the literature. The crystal structure of the title compound was analyzed by using experimental and theoretical methods.

Its crystal structure is confirmed with the aid of single crystal XRD analysis. It has been verified that (2E)-2-(3,4-Dimethoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one belongs to the Orthorhombic crystal system in the $P2_12_12_1$ space group with cell parameters $a=7.8906(7)$ Å, $b=9.4104(8)$ Å and $c=20.7764(19)$ Å, $\alpha=90^\circ$, $\beta=90^\circ$ and $\gamma=90^\circ$ in tune with its reported structure [290]. The crystal structure has been optimized using the Gaussian 09 software at the B3LYP/6-31++g(d,p) level. It is found that some of the calculated parameters are slightly deviated from experimental values, due to the fact that the theoretical calculations belong to isolated molecule in the gaseous phase and the experimental results belong to the molecule in the solid state. The linear regression analysis shows good agreement between the experimental and computed parameters.

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