CHAPTER 1

CRYSTAL GROWTH AND DENSITY FUNCTIONAL
THEORY–AN OVERVIEW

1.1 INTRODUCTION

Crystals have been admired by the mankind for their beauty. The exquisiteness of the crystals is due to their regular surface geometry and shiny colourful appearance. The gems and crystals delivered by the earth have often been formed at relatively low temperatures and crystallisation from solutions, in the course of hundreds and thousands of years. Natural crystals were kept as museum pieces and adored as gems in jewels. The transition of crystals from the museum to modern technology took place which has been the motivation for the crystal growing community for production of large crystals artificially. Since then major transformation has been effected in the electronics industry due to unique physical and chemical properties of grown crystals.

After the invention of transistor [Gilman 1963] crystal growth has become a commercial activity. Crystal growth is an art than a science and many efforts are being made to produce good crystals of desired materials [Stringfellow 1979]. It is the obligation of the crystal grower to produce a single crystal in large size from its poly-crystalline form by adopting the appropriate technique, as single crystals play a vital role in most of the applications.
Crystals are unacknowledged pillars of modern technology. Artificial research crystals of high quality are the basis of solid state research activities. They have become indispensable in many fields without which there would be no photonic industries, electronic industries, and no fibre optic communications. The current advancements in the fields of semiconductors, superconductors, polarizers, transducers, ultrasonic amplifiers, crystalline films of microelectronics, photosensitive materials, and computer industries can be credited to the strong influence of single crystals. Crystal growth is an essential part of material science and engineering, as crystal of suitable size and perfection are required for fundamental data acquisition and for practical devices and other application. Hence modern technology requires physicists, chemists, metallurgists, engineers and crystal growers to assist each other at many levels. [Laudise 1975]. The crystal growth can progress in the direction of success of solid state research and technology, only if it develops a proficiency in relating structure, bonding and other chemico-physical considerations of properties of desired interest.

Molecular organic crystals have become the subject of intense theoretical and experimental research as they exhibit different optical, electronic and mechanical properties. In this chapter, the fundamentals of various methods to grow good quality crystals and in particular the solution growth method are discussed. Further the development of various spectroscopic methods, such as NMR, X-ray and vibrational spectroscopy play a decisive role in the technological progress. Vibrational spectroscopy is well established theoretical, analytical and measurement technique for the identification, elucidation and evaluation of molecular vibrations. The
combined study of infrared and Raman spectra and quantum chemical calculations of molecular properties provide considerable information about conformers, equilibrium structures, the inter-atomic force fields, the hydrogen bonding and thermodynamic properties of organic molecules. Ab initio quantum chemistry can predict the electronic and geometric structures of molecules and also in the interpretation of experimental data without relying on the data. Density functional theory (DFT) is one such quantum chemical method which is a powerful tool that can support the experimental information. It is one of the most widely used methods for calculations of the structure of atoms, molecules, crystals, surfaces and their interactions. The work in this thesis concerns applying density functional theory of organic crystals and hence a brief introduction of DFT theory has also been explained.

1.2 CRYSTAL GROWTH METHODS

1.2.1 Introduction

Crystal growth has been a subject of interest for many years, but much of the progress in both the understanding and the technology has been inspired by the increasing commercial importance of the subject. The first theory of crystal growth was proposed in the late 19th century. Many theories such as surface energy theory, diffusion theory, surface absorption theory etc., have been proposed by investigators to explain the kinetics and mechanisms involved in the process of crystal growth. The improvement of the theories of crystal growth has thrown more light on the understanding of crystal growth phenomena. The methods of growing crystals are very wide and mainly
dictated by the characteristics of the material and its size [Buckley 1951]. Crystal growth is a controlled phase transformation from solid to solid, liquid to solid or from vapour to solid phase. The common principle in all these methods is the formation of a nucleus which grows into a single crystal by organizing and assembling ions or molecules with specific interactions and bonding.

Crystal growth techniques range from a small inexpensive one to a complex refined expensive one. Some basic methods of growing crystals include growth from melt, growth from vapour and growth from solution. There are different techniques in each method and can be found in books and also on reviews reported by Brice [1973] on melt, Henisch [1988] on gel growth, Faktor and Garret [1974] on vapour growth, Buckley [1951] on solution growth and Elwell and Scheel [1975] on high temperature solution growth. Among these solution growth is the easiest, simplest and least expensive method. Further, crystals grown from solutions are faceted and their look and form afford visual pleasure apart from being of educative value.

1.2.2 Growth from solution

The growth of crystals from solution is a vital process which can be extended from laboratory to industrial and scientific research. This method can be classified into the following categories as

- High temperature solution growth
- Hydrothermal growth
- Low temperature solution growth
- Gel growth

Amidst the various methods growth of the crystals from solution in particular the low temperature solution growth is most popular due to its versatility and simplicity. This method is well suited for the materials which undergo decomposition in high temperature or in the melt. Good quality crystals can be grown easily from solution at low or rather ambient temperature as the growth occurs close to equilibrium conditions. As the crystals reported in this thesis are grown by low temperature solution growth technique, the same is discussed here in detail.

1.2.2.1 **Low temperature solution growth**

One of the earliest methods is the growth of crystals from aqueous solution. Materials having moderate to high solubility in temperature range, ambient to 100°C at atmospheric pressure can be grown by low-temperature solution method. The interaction of ions or molecules of the solute and the solvent which in turn depends on the thermodynamic parameters of the process, temperature, pressure and solvent concentration plays key role in the mechanism of crystallization from solution [Chernov 1984].

1.2.2.2 **Solution, Solubility and supersolubility**

The growth of crystals from solution is mainly a diffusion-controlled process. Solubility gradient and super saturation are the two chief parameters for the solution growth process. Solubility gradient dictates the growth
procedure and the crystal grows by the access of the solute in the solution where the degree of supersaturation is maintained. Hence it is important to determine the solubility of the solute in the chosen solvent before starting the growth process [Christian 1990]. At a given temperature, a limited amount of solute dissolves in a particular solvent and is defined as solubility. The solubility of the substance is the function of the temperature of the solvent and it increases with increase in temperature for most of the materials. A saturated solution which is prepared at a certain temperature contains more amount of solute than the permitted level when cooled to a lesser temperature. The same thing happens, if a part of the solvent is allowed to evaporate. So, supersaturated solution is attained by cooling or evaporating the solvent from the solution. The solution is said to be in the supersaturated state, if the concentration of the solution is greater than the equilibrium concentration.

Low temperature solution growth is further divided into

- Slow evaporation method
- Temperature gradient method
- Slow cooling method

From all the above techniques, effective stirring of the solution is a required to obtain a good crystal. This is achieved either by rotating the crystal holder relative to the stationary solution or by rotating the solution around the crystal holder using a magnetic stirrer.
1.2.3 Methods of low temperature solution growth

1.2.3.1 Crystallization by slow cooling method

In this method the solution is allowed to cool to a lower temperature to obtain a supersaturated solution. Though it is one of the trusted methods the main drawback of this method is the need for a range of temperatures. Super saturation is attained by a change in temperature throughout the crystallizer. The use of a wide range of temperature might not be desirable because the properties of the grown crystals may vary with temperature. As the possible range of temperature are usually narrow most of the solute remains in the solution itself at the end of the growth. The major technical difficulty is this method is achieving the desired rate of cooling. This difficulty is overcome by using a thermostated crystallizer and the volume of the crystallizer is chosen based on the size of the crystal and the temperature dependence of the solubility of the substance. This method is adapted with great success using a programmable temperature controller. In general crystals produced by this method are small and their shapes are unpredictable.

1.2.3.2 Crystallization by temperature gradient method

The transport of the source materials from a hot region to a cooler region where the solution is supersaturated is the process involved in growth by the temperature gradient method. This method is insensitive to changes in temperature as long as both the source and the growing crystal undergo the same change. Even a small temperature difference between the source and the crystal zones has a greater effect on the growth rate. The main advantage of this method is the crystal can be grown at a fixed temperature and the cost effectiveness of the solute and the solvent.
1.2.3.3 Crystallization by solvent evaporation method

The slow solvent evaporation method is one which a part of the solvent is allowed to evaporate from the prepared solution. The main advantage of this method is that the growth of the crystals can be carried out at a fixed temperature. In this method the solution loses particles which are weakly bound to other components, and there is a decrease in volume of the solution. This is the oldest method of crystal growth and is a very simple technique. The vapour pressure of the solvent above the solution is higher than the vapour pressure of the solute and hence the solvent evaporates more rapidly making the solution supersaturated. Typical growth conditions involve a temperature stabilization of about 0.05°C and rate of evaporation of a few mm$^3$/h. But unpredictable fluctuation of the temperature still has a major effect on the growth of the crystal and this is overcome by the usage of a constant temperature bath. Evaporation of solvent from the surface of the solution produces high local supersaturation and formation of unwanted nuclei. Small crystals form on the walls of the vessel fall into the solution and affect the growth of the crystal. This can be eliminated by doing recrystallization and purification throughout the process.

1.3 CRITERIA FOR OPTIMIZING SOLUTION GROWTH

1.3.1 Material Purification

The choice of material of the highest purity is an essential prerequisite for success in crystal growth. Impurities in the material may be included into the crystal lattice causing flaws and defects in the formation of crystals. It
may also slow down the process of crystallization as being adsorbed on the growing face of the crystal causing changes in the crystal habit. The level of purity of the material has to be increased by standard purification methods such as recrystallization followed by filtration of the solution.

1.3.2 Selection of Solvent

It is important to select appropriate solvent for the solution growth. There may be different solvents for a given solute. The selection of good solvent has to be done taking into account the following factors:

- Good solubility for the given solute
- Good solubility gradient
- Less corrosion and non-toxicity
- Less viscosity and volatility of the solvent
- Small vapour pressure.

1.3.3 Preparation of solution

It is essential to have the solubility data of the material at different temperatures for solution preparation. The prepared solution is then filtered using the filter papers of different pore sizes to get a clear solution. For growth by slow cooling the clear saturated solution at a desired temperature is taken in a growth vessel and it is sealed to provide a controlled evaporation at a constant temperature. By varying the temperature, a situation where neither the occurrence of growth nor dissolution is established. Then the solution is tested for saturation by suspending test seed crystal in the solution. Necessary
equilibrium condition is achieved and the test seed crystal is removed and a fresh seed crystal is introduced for crystal growth.

1.3.4 Seed Preparation

Seed crystals are prepared by self-nucleation under slow evaporation from saturated solutions. The seeds of good visual quality, free from any inclusion of impurities and imperfections are chosen for growth. Strain free refaceting of the seed crystal decreases the dislocation content of the seed crystal and hence a few layers of the seed crystal are dissolved before initiating the growth.

1.3.5 Crystal habit

Almost all crystals grow approximately equivalent rates in all dimensions. Crystals which grow as needles or plates, the growth dislocations propagate along the principal growth directions and the crystals remain imperfect [Pamplin 1979]. Needle like crystals have very limited applications and plate like crystals need favourable orientation. The changes in the growth habit of needle and plate like crystals can be achieved either by changing the temperature of the growth or by changing the pH of the solution or by changing the solvent.

1.3.6 Merits of low temperature solution growth technique

The Low temperature solution growth method of crystal growth is popular because of its simplicity and versatility. The key advantages of solution growth techniques are
• Simple growth apparatus
• Growth of strain and dislocation free crystals
• The only method which can be used for substances that undergo decomposition before melting.
• Large size crystal can be grown

The two main limitations of this method is the growth substance should not react with solvent and this method is applicable to the substance which are fairly soluble in a solvent.

1.4 COMPUTATIONAL TECHNIQUES

1.4.1 Introduction

Quantum chemical computational methods have become a useful tool for solving interesting chemical problems and reaction mechanism. It has become a useful way to investigate materials to make predictions before running the actual experiments that are too difficult or too expensive. Due to explosive developments in computer hardware and associated achievements, quantum mechanical methods can now be directly applied for various scientific applications. Computational quantum chemistry is primarily concerned with the numerical computation of molecular electronic structures by ab initio and semi-empirical techniques. Computational methods, especially ab initio have become a major tool in the study of molecular problems of structure, stability and reaction mechanism [Lipkowitz et al. 2007, Lorenc et al. 2008].
Some common computer softwares used for computational chemistry are GAUSSIAN, GAMESS, MOPAC, etc. The Gaussian is the most widely used program package for performing electronic structure calculations. Computations of optimized molecular geometry and vibrational spectra are normally carried out with input as the molecular structure provided in the Z-matrix format or in Cartesian co-ordinate form. In the present work Gaussian 03 package is used for structural optimization and to find the related parameters for further understanding about the molecules considered.

Quantum chemical calculations provide useful data, which complements experimental data on the structures, properties and reactions of molecules. The calculations are based primarily on Schrödinger equation for generating electronic and charge distributions, molecular geometry in ground and excited state, spectral wavenumbers (IR, Raman, NMR and UV-Vis spectra), potential energy surfaces, thermodynamic calculations (heat of reactions, energy of activation) and other observable properties (dipole moments, polarizability, etc.). These results are particularly useful for determination of properties that are experimentally inaccessible and interpretation of experimental data is complicated.

For polyatomic molecules, the presence of several nuclei makes quantum mechanical calculations more complex than for diatomic molecules. Moreover, the electronic wave function of polyatomic molecules depends on several parameters like bond distances, bond angles and dihedral angles.
There are two main approaches for calculating molecular structure and their reactivity. They are molecular mechanics and electronic structure theory.

In molecular mechanics simulations, the laws of classical physics are used to predict the structures and properties of molecules. In this method, it does not explicitly treat the electrons in a molecular system. Instead, the computations are performed based on the interactions among the nuclei. Electronic effects are implicitly included in force fields through parameterization. This method can be used for very large systems containing thousands of atoms.

Electronic structure methods are based upon the fundamental laws of quantum mechanics, which are characterized by their various mathematical approximations to its solution. There are three major classes of electronic structure methods: Viz., semi-empirical methods, ab initio methods and density functional methods [Cotton 1971].

1.4.2 Ab initio method

The term ab initio in Latin is “from the beginning”. Methods that do not include any empirical or semi-empirical parameters in their equations, being derived directly from theoretical principles with no inclusion of experimental data, are called ab initio methods. This does not imply that the solution is an exact one; they are all approximate quantum mechanical calculations. It means that a particular approximation is rigorously defined on first principles (quantum theory) and then solved within an error margin that is qualitatively known beforehand.
The Schrödinger’s equation is transformed into a set of Hartree-Fock (HF) equations. The simplest type of ab initio electronic structure calculation is the HF scheme, an extension of molecular orbital theory, in which the correlated electron-electron repulsion is not specifically taken into account; only its average effect is included in the calculation. As the basis set size is increased, the energy and wave function tend towards a limit called the Hartree-Fock limit. The Hartree-Fock wave function is a single configuration or determinant. In some cases, particularly for bond breaking processes, this is quite inadequate, and several configurations need to be used. Here, the coefficients of the configurations and the coefficients of the basis functions are optimized together. The primary deficiency of HF method is that the correlation of electron motion cannot be accounted adequately. Hartree-Fock theory is very useful for providing initial, first-level predictions for many systems. It is also reasonably good in computing the structures and vibrational frequencies of stable molecules and some transition states.

1.4.3 Density Functional Theory method

Density functional theory (DFT) is a quantum mechanical modelling method used in physics and chemistry to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. With this theory, the properties of a many-electron system can be determined by using functional, i.e. functions of another function, which in this case are the spatially dependent electron density. Hence the name density functional theory comes from the use of functionals of the electron density. Once the electron density is known the
external potential and consequently the Hamiltonian, the wave function calculated may be used to determine the desired molecular properties. One popular function is known as BLYP (from the name Becke for the exchange part and Lee, Yang and Parr for the correlation part). Even more widely used is B3LYP which is a hybrid functional in which the exchange energy from Becke’s exchange function is combined with the exact energy from Hartree-Fock theory. Along with the component exchange and correlation functionals, three parameters define the hybrid functional, specifying how much of the exact exchange is mixed in. Unfortunately, although the results obtained with these functions are usually sufficiently accurate for most applications, there is no systematic way of improving them. Hence in the current DFT approach, it is not possible to estimate the error of the calculations without comparing them to other methods or experiments.

DFT is among the most popular and versatile methods available in condensed matter physics, computational physics, and computational chemistry. DFT methods are attractive because they include in their model the effect of electron correlation and hence receive ever-increasing popularity in the chemical community due to its capability to treat electron correlation with low computational cost.

1.4.4 Semi-empirical method

Semi-empirical methods use parameters derived from experimental data or the results of ab initio calculations [Dewar and Reynolds 1986]. They solve an approximate form of the Schroedinger equation that depends on
having appropriate parameters available for the type of chemical system under investigation. They are very important in computational chemistry for treating large molecules where the full Hartree-Fock method without the approximations is too expensive. The use of empirical parameters appears to allow some inclusion of electron correlation effects into the methods. Within the framework of Hartree-Fock calculations, some pieces of information (such as two-electron integrals) are sometimes approximated or completely omitted. To compensate this loss, semi-empirical methods are parameterized, that is their results are fitted with a set of parameters, normally in such a way as to produce results that best agree with experimental data, but sometimes to agree with ab initio result.

1.4.5 Basis sets

A basis set is a mathematical description of the orbitals within a system used to perform theoretical calculations [Jensen 1999]. The basis set can be interpreted as restricting each electron to a particular region of space. Larger basis sets impose fewer constraints on electrons and approximate each orbital more accurately but require more computational resources. The standard basis sets for electronic structure calculations use linear combinations of basis functions to form the orbitals. The individual molecular orbital is defined as:

$$\varphi_i = \sum_{\mu=1}^{n} C_{\mu} \chi_{\mu}$$

Where, $\varphi$ is the $i^{th}$ molecular orbital, $C_{\mu}$ is the coefficients of linear combination and $\chi_{\mu}$ is the $\mu^{th}$ atomic orbital and $n$ is the number of atomic orbitals.
Gaussian and other ab initio electronic structure programs use basis functions which themselves are composed of a linear combination of Gaussian functions and such basis functions are referred to as contracted functions, whereas the component Gaussian functions are referred to as primitives. A basis function consisting of a single Gaussian function is termed as uncontracted. The Gaussian program package offers a wide range of predefined basis sets, which may be classified by the number and type of basis functions that they contain.

The smallest possible basis set representation is termed as minimal or single zeta basis set and they use fixed-size atomic-type orbitals. The STO-3G basis set is a minimal basis set. Split valence basis sets, such as 3-21G and 6-31G, have two (or more) sizes of basis function for each valence orbital and allow orbitals to change size, but not to change shape where the description is split into an inner component describing the core electrons with one level of representation. Triple split valence basis sets, like 6-311G, use three sizes of contracted functions for each orbital-type. Additional improvements of the basis set can be achieved by adding polarization functions or diffuse functions.

By adding orbitals with angular momentum beyond what is required for the description of each atom in the ground state, the polarized basis sets allow orbitals to change the shape. The 6-31G (d) basis set also known as 6-31G* which contains the d-functions added to the heavy atoms, is becoming very popular for calculations involving up to medium-sized systems.
Diffuse functions are large size versions of s- and p-type functions (as opposed to the standard valence-size functions). They allow orbitals to occupy a larger region of space. Basis sets with diffuse functions are important for systems where electrons are relatively far from the nucleus like molecules with lone pairs, anions and other systems with significant negative charge, systems in their excited state, systems with low ionization potentials, and so on. The 6-31+G (d) is the 6-31G (d) basis set with diffuse functions added to heavy atoms.

The choice of basis set is very important for the quality of the computational results. A sufficiently flexible and well-balanced basis set must be used to obtain accurate results, but accuracy and computational cost has to be weighed against each other.

1.4.6 Geometry optimization

Generally structural changes within the molecule produce differences in its energy and other properties. Its potential energy surface specifies the way the energy of a molecular system varies with small changes in its structure. The potential energy surface is just a mathematical relationship correlating the particular molecular structure and its single point energy. They are usually represented by three dimensional plots and they are characterized by distinct points:

A local maximum is the point on the potential energy surface and is the highest value in a particular section or region of the PES.
A Global maximum is the point on the potential energy surface and is the highest value in the entire PES.

Saddle point – a point on the potential energy surface that is a maximum in one direction and a minimum in the other direction. Saddle points represent a transition structure connecting two equilibrium structures. The minimum specifies the equilibrium structure of the molecular system with different minima corresponding to different conformations. After finding the energy and gradient in a number of cycles, finally optimization gets completed when it has converged.

1.4.7 Molecular vibrations

A molecular vibration occurs when atoms in a molecule are in periodic motion while the molecule as a whole has constant translational and rotational motion. The frequency of the periodic motion is known as a vibration frequency. Molecular vibrations are important in understanding infrared absorption and the mechanisms and kinetics of chemical reactions. In general, a molecule with N atoms has 3N-6 normal modes of vibrations, but a linear molecule has 3N-5 such modes, as rotation about its molecular axis cannot be observed. The normal modes of vibration of polyatomic molecules are independent of each other but each normal mode will involve simultaneous vibrations of different parts of the molecule such as different chemical bonds. A molecular vibration is excited when the molecule absorbs a quantum of energy, \( E = \hbar \nu \), corresponding to the vibration frequency, \( \nu \) (where \( \hbar \) is
Planck’s constant). A fundamental vibration is excited when one such quantum of energy is absorbed by the molecule in its ground state.

### 1.4.8 Frequency calculations

The vibrational states of a molecule are observed experimentally by infrared and Raman spectroscopy. These techniques can help to determine molecular structure and environment. In order to collect this useful information, it is necessary to determine what vibrational motion corresponds to each peak in the spectrum. This assignment can be quite difficult due to the large number of closely spaced peaks possible even in fairly simple molecules. Therefore computer simulations are used to calculate the vibrational frequency of molecules which helps in the assignment. Gaussian can compute the vibrational spectra of molecules in their ground and excited states. This program can also describe the displacements of the system in its normal mode. It can predict the direction and magnitude of the nuclear displacement that occurs when a system absorbs quantum of energy. Frequency calculations are valid only at stationary points on the PES, and the frequency calculations must be performed on optimized structures.

### 1.4.9 Natural Bond Orbital (NBO) analysis

A natural bond orbital (NBO) analysis is an effective technique for studying hybridization and covalence effects in polyatomic wave function, based on local block eigenvectors of the one-particle density matrix. NBO analysis is based on a method for optimally transforming a given wave function into localized form, corresponding to the one-centre (lone pairs) and
two-centre (bonds) elements of the chemist’s Lewis structure picture. An optimal Lewis structure can be defined as that one with the maximum amount of electronic charge in Lewis orbitals (Lewis charge). A low amount of electronic charge in Lewis orbitals indicates strong effects of electron delocalization. The NBOs are one of a sequence of natural localized orbital sets that include Natural Atomic Orbitals (NAOs), Natural Hybrid Orbitals (NHOs), Natural Bonding Orbitals (NBOs) and Natural (semi-) Localized Molecular Orbitals (NLMOs). These natural localized sets are intermediate between basis atomic orbitals (AOs) and molecular orbitals (MOs):

Atomic orbital $\rightarrow$ NAO $\rightarrow$ NHO $\rightarrow$ NBO $\rightarrow$ NLMO $\rightarrow$ Molecular orbital

Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBOs and formally unoccupied (antibond or Rydberg) non-Lewis NBOs, corresponds to a stabilising donor – acceptor interaction, which is taken into consideration by examining all possible interactions between filled (donor) and empty (acceptor) orbitals, and then evaluating their energies by second order perturbation theory.

1.4.10 HOMO and LUMO orbitals

HOMO and LUMO are acronyms for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively. The analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground state to the first excited state and is mainly described by one electron excitation form the highest occupied molecular orbital to the lowest unoccupied molecular orbital. The energy difference
between them is termed as HOMO – LUMO energy gap. The HOMO, LUMO are sometimes referred to as frontier orbitals. HOMO as an electron donor represents the ability to donate an electron, while LUMO as an electron acceptor represents the ability to obtain an electron. The eigenvalues of LUMO and HOMO and their energy gap reflect the chemical activity of the molecule. Fukui [1982] reported that a good approximation for reactivity could be found by looking at the frontier orbitals (HOMO/LUMO) based on three main observations of molecular orbital theory as the two molecules interact:

- The occupied orbitals of different molecules repel each other.

- Positive charges of one molecule attract the negative charges of the other.

- The occupied orbitals of one molecule and the unoccupied orbitals of the other interact with each other causing attraction.

From these observations, frontier molecular orbital (FMO) theory simplifies reactivity to interactions between the HOMO of one species and the LUMO of the other. For the HOMO of one molecule to interact with a LUMO of another, the symmetry must be correct. If the symmetry is wrong, there will be no interacting orbitals and the reaction is favoured by a lower HOMO – LUMO gap.
1.4.11 Molecular electrostatic potential

Electrostatic potential correlates with dipole moment, electronegativity and partial charges. It provides a visual method to understand the relative polarity of a molecule. Electrostatic potential maps are very useful for three dimensional diagrams of molecules. They enable us to visualize the charge distributions of molecules and charge related properties of molecules. They also allow us to visualize the size and shape of molecules. In organic chemistry, electrostatic potential maps are invaluable in predicting the behaviour complex molecules. The first step involved in creating an electrostatic potential map is collecting a very specific type of data: electrostatic potential energy. An advanced computer program calculates the electrostatic potential energy at a set distance from the nuclei of the molecule. Electrostatic potential energy is fundamentally a measure of the strength of the nearby charges, nuclei and electrons at a particular position. Large quantity of electrostatic potential energy values must be calculated to analyse the charge distribution of a molecule. So, to make the electrostatic potential energy data easy to interpret, a colour spectrum is employed to convey the varying intensities of the electrostatic potential energy values.

1.5 INTERMOLECULAR INTERACTIONS

In recent years, molecular organic crystals have become the subject of intense theoretical and experimental research as they exhibit different optical, electronic and mechanical properties quite different from conventional solid covalent or ionic crystals. Crystal engineering is related to the building of
crystal structures of organic and metal organic species, using design principles that are the derived from the understanding of the intermolecular interactions that prevail in molecular solids [Desiraju 1989]. A variety of intermolecular interactions have been used in crystal engineering like electrostatic, hydrogen bonding, van der Waals and $\pi-\pi$ stacking. Among these understanding the strength, directionality, and selectivity of hydrogen bonding is the primary aim of the research efforts in the design of supermolecules and crystal engineering [Lehn 1995]. The understanding of hydrogen bonds is necessary because it is both strong and highly directional [Jeffrey 1997]. Among the large variety of hydrogen bonds the strong variety is O-H...O and N-H...O and there are also weaker varieties like C-H...O, C-H...$\pi$ and other varieties that incorporate metal atoms, multiple atom acceptors [Desiraju and Steiner 1999] These hydrogen bonds have a greater or lesser influence of the outcome of the final crystals. The perfect example for this is the chicken-wire structure of the 1:1 molecular complex of melamine and cyanuric acid where the hydrogen bonds give rise to a layered crystal structure. Interestingly melamine and its organic and inorganic complexes or salt form supramolecular structures by the formation of strong N-H...O, N-H...N and O-H...O bonds. The structural arrangement is a result of number of intermolecular arrangements, hydrogen bonds forming chain structures, accompanied by $\pi-\pi$ interactions reinforcing the formation of the layered structure. The net effect of all the hydrogen bonds is to form a three dimensional network. Thus the weak intermolecular interactions such as hydrogen bond play an important role in the construction of new crystals.
1.6 A REVIEW OF MELAMINE BASED COMPOUNDS

Melamine (C₃N₆H₆) is an industrially synthesized chemical which becomes an integral part of our daily life. It is used in dinnerware, laminates, speciality coatings for paper and textiles. Melamine has a very similar structure to well known aromatic explosive, Triamino trinitro benzene (TATB). But melamine will not combust or does not burn very well. Such a disparity between the two compounds behaviour where one is an explosive and other is a fire-retardant. The uniqueness of melamine (2,4,6-triamino-s-triazine) lies in the symmetrically positioned three reactive amino groups on an extremely stable triazine ring.

![Structure of melamine](image)

**Fig.1.1. Structure of melamine**

The high nitrogen content of melamine has enabled melamine to be detected as a fake protein. The recent adulterated infant milk food epidemic in China is due to the addition of melamine to milk powder as a cheap protein additive.

Melamine is mainly an industrial chemical. Its derivatives have increased the variety of cross-linking agents available for coating
formulations and the technology is suitable for water borne, solvent-based and powder coating systems [Wicks et al. 1992a, 1992b]. The crystals, including melamine salts, reveal interesting properties like non-linear optical behaviour, liquid crystalline polymers and toxicity. Melamine molecule is known as an effective unit for self-assembled supramolecular structures both organic-inorganic and organic-organic types. Good physical and chemical stability is connected with the existence of the inorganic part in investigating compounds, whereas the organic part is responsible for nonlinear optical properties. In the variety of newly designed crystals, the melamine occurs in singly, doubly and triply protonated cations.

In the recent years much attention has been paid to the vibrations of melamine and melamine based compounds. The fundamental frequency assignment of melamine and melamine $d_6$ was done almost 50 years ago by Jones and Orville-Thomas [1959]. They reported the IR spectrum and assigned most of the in-plane normal modes assuming $D_{3h}$ symmetry for the melamine molecule. X-ray diffraction studies have been done to study the crystal structure of melamine at room temperature [Hughes 1961, Larson and Cromer 1974]. Later, Raman spectrum of the solid sample of the molecule was reported and some bands in the low energy region were assigned by Sawodny et al. [1966]. The complete normal coordinate analysis of the elementary cell of the crystal melamine was reported by Schneider and Schrader [1975] by analysing the inner vibrations of the molecules and the vibrations of the lattice and also the influence of the molecules on each other. Meier et al. [1995a] reported the new methodology to the interpretation of the vibrational spectrum of melamine molecule. They determined the quantum
energy surface to obtain the functional form and the initial set of force constants of the molecule and used it in the interpretation of vibrational assignments. They also reported the assignments of few fundamentals and gave the form of some of the normal modes of methylol melamines and bridged methylol melamine compounds [Meier et al. 1995b]. Further, the theoretical vibrational calculation of the melamine molecule was reported by Wang et al. [1997] at the ab initio (MP2) and several density functional theory (DFT) schemes with different basis sets. The main molecular properties of melamine are characterized by the interaction between $\pi$-electron in the triazine ring lone-pair electrons in the amino-nitrogen. Larkin et al. [1998] studied the mechanical coupling of substituent vibrations with triazine ring modes of melamine derivatives and gave the detailed vibrational analysis of those derivatives. Fernandez et al. [2001] reported the vibrational dynamics of melamine molecules by measuring inelastic neutron scattering spectrum of melamine and normal coordinate analysis. The vibrational and NLO properties of neutral melamine and also singly, doubly and triply protonated melaminium cations were studied by Drozd and Marchewka [2005]. It was reported that during protonation there is a systematic change in the C-N bonds. The C-N bonds between the ring and the amine group contract whereas the opposite trend is noticed for C-N bonds in the triazine ring due to the attachment of the proton in the next position. Lamers et al. [1997] reported that ambient air ultraviolet light irradiation of acrylic-melamine and polyester-melamine based clearcoats significantly improves the acid etch resistance of the coating without changing any of the properties of bulk coating material. There is still growing interest in the study of crystals
containing melaminium cation. As an excellent hydrogen donor and hydrogen acceptor, melamine a famous organic base forms a variety of dimensional networks in combination of various carboxylic acids.

Several researches have been done on complexes formed with melamine molecule and have already been reported. Zerkowski et al. [1990] reported that 1:1 cocrystals of derivatives of melamine and barbituric acid. These cocrystals have interesting structures of infinite hydrogen bonded tapes that run parallel to the axes. Crystals of tetrakis (2,4,6-triamino-1,3,5 triazin-1-ium) bis(selenate) trihydrate and 2,4,6-triamino-1,3,5-triazin-1,3-ium tartrate monohydrate exhibiting second harmonic generation was reported by Marchewka et al. [2003a, 2003b]. Generally the formation of melamine complexes with various carboxylic acids has a feature of the self-organization process in which the anion acts a bridge that actively associates with the cationic layer through intermolecular interactions. Vibrational analysis of several singly protonated melaminium compounds like melaminium chloride hemihydrate, melaminium citrate, melaminium 2,5-dinitrophenolate monohydrate, melaminium hydrogen phthalate, has been studied by Marchewka et al. [2002-2004,2011a]. Non covalent synthesis such as hydrogen-bonding, metal coordination, ionic interactions has received considerable attention. The metal compounds of melamine that have been reported to date are almost limited to group II metals. There is very little literature available of the same. Austin et al. [2006] has studied the coordination of chemistry of copper salts with melamine. Yu Qui and Lian Gao [2005] reported the photo luminescence studies of blue emitting cyanuric acid melamine complex which was prepared from thermolysis of urea in a
two step method. The study reveals that a relatively strong and pure room-temperature blue-light emission band at 470 nm. Moreover it was found that the complex has a good thermal stability making it suitable for using as an organic light emitting diode material.

Thus the trimer of cynamide i.e. melamine represents an interesting molecule from the point of view of crystal engineering and supramolecular chemistry. Melamine finds its application in the field of reinforced plastics also. Sheet moulding compound (SMC) a composite material used in the automotive industry. The SMC market is dominated by one-component acrylic melamine systems [Renault 2001, Drago 2000, Demez 1995]. Melamine finds its use in chemical modification of starch which is used to obtain products that are capable or removing heavy-metal ions from industrial waste water. Khalil and Abdel-Halim [2000] showed that the mono methylol and dimethylol resins based on melamine can react with maize starch as a tridentate ligand yielding a neutral derivative. Recently Binoy et al. [2013] performed the DFT analysis of melaminium formate complex and also had suggested a new mechanism of proton transfer responsible for NLO activity based on anomalous IR spectral bands in the high wavenumber region. DFT computational studies of melaminium nitrate and vibrational spectral investigations of melaminium maleate monohydrate by quantum chemical calculation have been reported recently by Arjunan et al. [2013], and Hasan Tanak and Marchewka [2013].
1.7 SCOPE OF THE THESIS

Crystal engineering is an interesting design of functional and molecular solids from neutral and ionic building blocks, using intermolecular interactions in the design strategy. The expansion of crystal engineering during the recent years as a research field has thrown significant interest in the origin and nature of intermolecular interactions and their use in the design and preparation of new crystalline structure. In this aspect attempts have been made to grow two new organic-organic crystal of melamine-3-nitrophenol (3-NPM) and melamine-acrylic acid complex (MAC). The thermal behaviour and dielectric properties of the same has been done. Spectroscopy is an effective tool to understand the structure, functional groups and nature of molecular framework present in the molecule and also about the nature of chemical bonds involved. Hence FT-IR, FT-Raman, equilibrium geometry, various bonding features and harmonic vibrational frequencies of 3-NPM and MAC has been investigated with the help of B3LYP density functional theory (DFT) using 6-311G (d, p) and 6-31G (d, p) as basis set. The growth and characterization of melaminium bis (trifluoroacetate) trihydrate (MTFA) by the slow evaporation technique is done and has been characterized through single crystal XRD, FTIR, FT-Raman, FT-NMR, UV-Vis, Thermal, microhardness, laser damage threshold, dielectric studies, SHG conversion efficiency. Further structural and spectroscopic analysis of MTFA has been made by density functional harmonic calculations using DFT/6-311G (d, p) basis set. Thermo gravimetric analysis is an effective technique to determine characteristics of thermal decomposition kinetics and thermal stability of the polymer and its composite. The multiple heating rate method is recommended
for estimating the kinetic parameters for the thermal decomposition of polymer composites. The thermal decomposition of melaminium phthalate (MPH) and melaminium bis(hydrogen oxalate)(MOX) compounds has been studied by thermogravimetric analysis at three different heating rates: 10, 15 and 20°C/min. Further MPH and MOX are also characterized by FT-IR, FT-Raman, FT-NMR and dielectric studies. The DFT calculation of MOX has been done using 6-311++G (d, p) basis set.