Chapter 1

INTRODUCTION

1.1 Motivation:

A prolonged era believed that all optical properties in any medium are linear, but soon after the discovery of Ruby laser in 1960 [1] the notion started to change. Franken *et al.* [1b], with their demonstration of Second Harmonic generation showed the first nonlinear optical (NLO) properties of material using a laser. This fascinating phenomenon of nonlinear optics literally opened up a technological revolution.

Inorganic semiconductor and semiconductor-insulator systems dominated the materials science research, for e.g., KDP (Potassium dihydrogen phosphate), DKDP (potassium dideuterium phosphate), ADP (ammonium dihydrogen phosphate), cadmium sulfide, BBO (*ß*-BaB_2O_4), LBO (LiB_3O_5), Cesium lithium borate (CLBO), potassium titanyl phosphate (KTP), lithium tetraborate (LTA), lithium niobate (LiNbO3). Fig. 1.1 illustrates the CLBO crystal; frequency doubled Nd:YAG Laser System and green light generation by sending infrared light into a NLO active crystal (bottom). KDP, DKDP and ADP are widely used as the second, third and fourth harmonic (4HG, output at 266 nm) generators for Nd:YAG laser at 1064 nm. Inorganic crystals face problem to tune the response time and magnitude of the optical nonlinearity at a time [2-5].

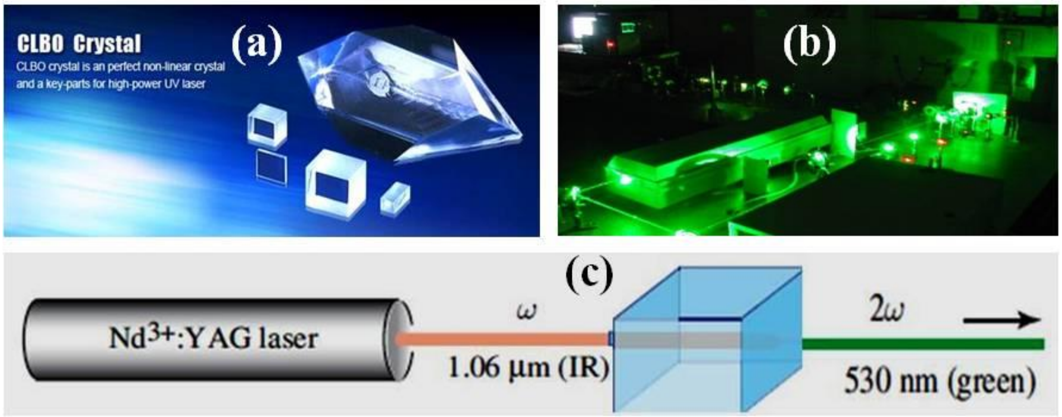


Figure 1.1: (a) CLBO crystal, **(b)** frequency doubled Nd:YAG Laser System and **(c)** generation of green light by sending infrared light into a NLO active crystal.

Since last three decades, focus has been shifted towards the organic compounds due to their advantages in design flexibility, high optical damage thresholds, optical speed and efficiency over inorganic materials. Some organic materials even exhibited second-harmonic generation (SHG) efficiencies that undoubtedly exceed those of inorganic NLO crystals such as ($LiNbO_3$) or (KDP). Sooner or later organic NLO materials shall be able to replace inorganic materials as electro-optic modulators and optical switches used in industrial applications. The quest and development of environment friendly new materials is necessary to improve the technology, but any approach that reduces the cost of material development is indeed preferred, which is a challenge. Hence, new NLO materials are needed to extend the range of photonic applications [6-14].

1.2 Linear optics:

To experience the essence of NLO one has to begin the discussions with linear optics. Linear optics is considered with the processes of weak light (applied electric field $< 10^5$ V/m), where light is deflected or delayed but its frequency is untouched. This linear optical process is related to the energy (or wavelength) of the radiation, but not on the intensity. The refractive index and absorption coefficient are independent of light intensity but principle of superposition is applicable. Despite the fact the frequency remains unaltered with the passage of light in a medium. Two beams of light in the same region of a medium do not interact and affect each other; these properties can be seen in phenomena like reflection, transmission, absorption, fluorescence etc. To deal with such phenomena on the atomic scale, light is treated as a quasi - particle: *Photon* (Quanta of light). **Absorption** looks at the number of absorbed photons (intensity) vs. photon frequency ω. **Reflection** looks at the number of reflected photons (intensity) vs. photon frequency ω**.** **Transmission** tells the number of transmitted photons (intensity) vs. photon frequency ω. **Emission** considers the number of emitted photons (intensity) vs. photon frequency ω.

Some application of linear optics in daily life is shown in Fig. 1.2, which includes the phenomena of total internal reflection, using fluorescence wonderfully in rescue operation and Dichroic filters.

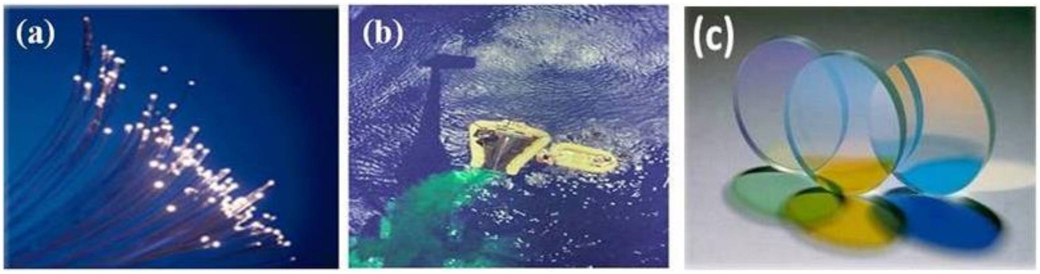


Figure 1.2: (a) Optical fiber for communication-application of total internal reflection, **(b)** to aid location, the Gemini 4 spacecraft releasing fluorescein into water and **(c)** Dichroic filters are created using optically transparent materials.

An incident electromagnetic field induces dipole moments (***P***) inside the optical medium.

$$\boldsymbol{P} = \epsilon_0 \chi \boldsymbol{E} \tag{1.1}$$

Where, ϵ_0 is the permittivity of free space, χ is the electric susceptibility and $\boldsymbol{E}$ is the electric field inside the medium [15, 16].

1.3 Nonlinear Optics:

Nonlinear effects are valuable for countless systems and device applications**:** optical switching, soliton formation, frequency up conversion giving access to spectral ranges like the visible or ultraviolet (UV), a key piece of space-based Light Detection And Ranging (LIDAR) systems, broadband amplification, optical fibers etc. An excellent review by Garmire in 2013 highlighted the use of NLO in daily life. Few interesting events worth mentioning is highlighted in the following section.

Lasers using phase change NLO processes with addition or removal of materials can eternally transform it. Application of these processes are used in semiconductor industry to eliminate conducting Indium tin oxide (ITO) electrodes on solar cell edges, to remove short circuits, for trimming resistors, drilling and structuring of printed circuit board, to mark LED chips etc. Very minute change in surface texture, shape and dimensions can impinge on the performance in surgical tools and for implantation. The required advanced manufacturing process is fulfilled by ultrafast lasers which provide exceptionally high accuracy with quality as it works without heat dissipation. New generations of coronary stents, surface textured bio-implants, catheters are available for use. NLO attaches itself in real-time 3D image formation using nonlinear refractive index / absorption, or both of a chromophore. Therefore, telepresence, telemedicine, advertising, prototyping is possible with NLO [17, 18].

NLO is considered to be the optics of intense light (applied electric field is between 10^5 - 10^8 V/m). The observed effects are induced by light itself as it propagates through the medium. Superposition principle does not hold here. In an applied optical wave, when E is large, the response (nonlinear) of an optical material is described by expressing the material polarization ***P(t)*** as a power series expansion of the electric field ***E(t)***, as

$$\boldsymbol{P}(t) = \epsilon_0 (\chi^{(1)} \boldsymbol{E}(t) + \chi^{(2)} \boldsymbol{E}^2(t) + \chi^{(3)} \boldsymbol{E}^3(t) + \cdots). \tag{1.2}$$

Where, $\chi^{(1)}$ is first order susceptibility; $\chi^{(2)}$ is the second order susceptibility, illustrates processes as second harmonic generation; $\chi^{(3)}$ is the third-order susceptibility, practices two-photon absorption, third harmonic generation, reverse saturable absorption (RSA), intensity-dependent refractive index etc and so on [6, 19-23]. Fig. 1.3 schematically represents behavior of linear and nonlinear optical polarization.

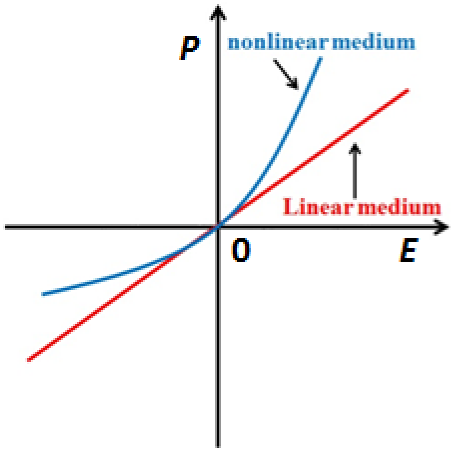


Figure 1.3: Polarization as a function of electric field in a linear and nonlinear medium.

A material that has a nonlinear relationship between polarization and the electric field is a nonlinear medium and the branch of optics that studies and explores this property is known as nonlinear optics. Electric field strength in the order of 10^3 V/cm can be achieved by conventional light sources. The field of these light sources does not influence the atoms, as the inter-atomic field strength is in the range of 10^7 - 10^{10} V/cm. So, the medium behaves linearly. Intense laser radiation generates field of 10^8-10^9 V/cm strength. The atoms are affected by this high field which results in induced dipole oscillations with higher amplitudes.

The Eqn. (1.2) is applicable to materials having instantaneous response. Materials having a non zero $\chi^{(2)}$ with amply large applied field shows a quadratic relationship of polarization [24-26]. In the context of NLO materials, two types of absorption processes are relevant – linear & nonlinear absorption.

1.4 Linear Absorption:

An energy level diagram explaining the linear absorption by the chromophore molecules is shown in Fig. 1.4. Absorption in NLO chromophores takes place because of charge transfer energy gap. When they face radiation of energy above their charge transfer energy gap, the molecules in the ground state (S_0) are excited to a singlet state (S_1). S_1 has a life time of the order of nanosecond (ns). Molecules in the S_1 emit a large amount of the energy via fluorescence and return to S_0.

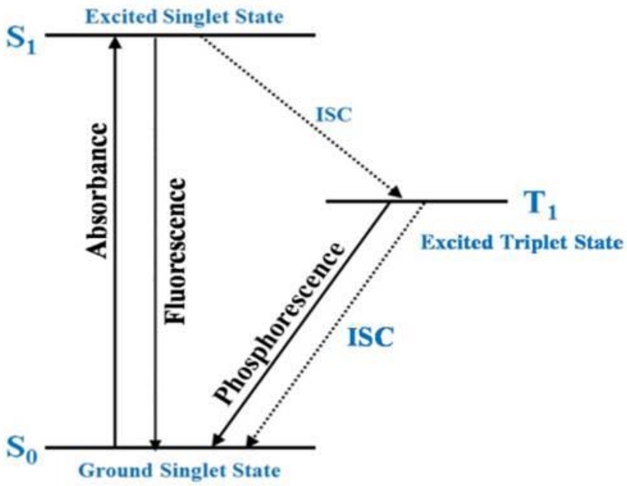


Figure 1.4: Energy level diagram displaying excitation of chromophores.

A small portion of the molecules in the S_1 decays to the excited triplet state (T_1), this spin forbidden state has a relatively long life time in comparison to S_1. Via a non radiative transition T_1 returns to S_0. ISC represents inter system crossing [27].

1.5 Two-Photon Absorption (TPA)

TPA is simultaneous absorption of two photons from the ground state of the molecule to an excited state through an intermediate virtual state. The photons may have different frequency. Fig. 1.5 shows the TPA process. The strength of absorption depends on the square of the light intensity, in this way it is different from linear absorption. The virtual state can be assumed just as a real state & lifetime approaching zero. The energy difference between the lower and upper states of the molecule is equal to the sum of two photon energies [28, 29]. TPA is a third order process. The imaginary part, $\chi^{(3)}$ of the third order nonlinear susceptibility is related to the scope of TPA in a given molecule. At low intensities, if the linear transmission is high, there will be no or diminutive ground state absorption. But as intensity increases two photons can together promote the molecule to an excited state.

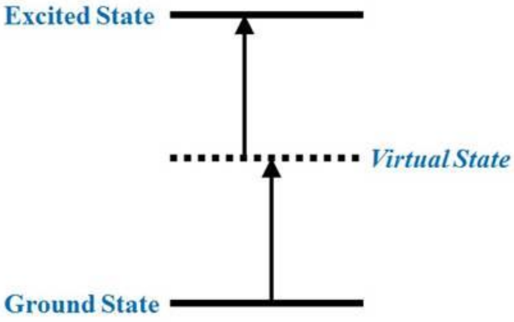


Figure 1.5: Schematic diagram of TPA process.

The TPA coefficient, β, is related to the imaginary part of $\chi^{(3)}$ through the Eqn. 1.3:

$$\beta = (3\omega / 2\varepsilon^0 c^2 n_0^2) Im [\chi^{(3)}]. \qquad (1.3)$$

Where, ω is the circular frequency of the light, ε^0 is the dielectric constant, *c* is the speed of light in vacuum and n_0 is the linear index of refraction.

The intensity of a beam as it passes through the material is given by Eqn. 1.4:

$$\frac{dI}{dz} = -[\alpha + \beta I] I \qquad (1.4)$$

Where, α is the linear absorption coefficient and β is the two photon absorption coefficient. If a material is transparent at low intensities, α = 0, the change in intensity of the light propagating through a material is given by Eqn. 1.5 [30].

$$I(L) = I_0 / (1 + I_0 \beta L) \qquad (1.5)$$

Where, *L* is the sample length and I_0 is the incoming intensity.

Eqn (1.5) shows that, as the intensity (I_0) increases the transmission decreases, so it is correlated with the material thickness, intensity, TPA coefficient. The intensity ought to be very high in order to witness any optical limiting effect due to TPA, as most materials possess a rather small β value.

The band gap energy is the energy difference between the HOMO and LUMO also controls the TPA coefficient. The relation between band gap energy and β is given by,

$$\beta(\omega) = K(E_p^{1/2}/n_0^2 E_g^3)\ F\ (2\hbar\omega/E_g) \qquad (1.6)$$

Kane energy parameter E_p is material independent for direct band gap material; K is a material independent constant and E_g is the band gap energy. Eqn. 1.6 shows that a large E_g has negative effect on the TPA coefficient and β has a frequency dependence which is weaker compared to one-photon absorption [31].

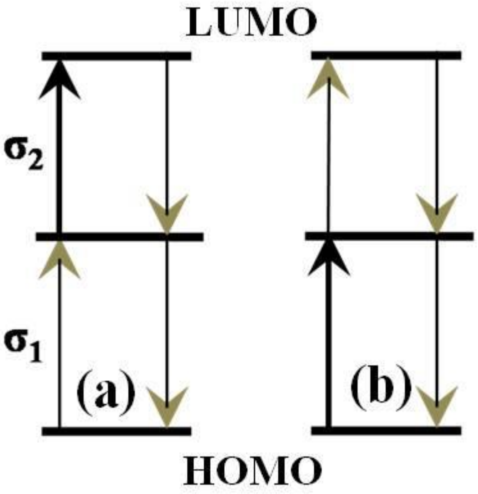


Figure 1.6: (a) Electronic process of saturable absorption and **(b)** RSA process, the excited state cross section **σ_2** is larger than the ground state absorption **σ_1**.

1.6 Saturable absorption:

When the incident intensity is high enough that the ground state population depletes the population of the upper and lower states equalizes and saturable absorption occurs. As the frequency of incident light is close to an absorption resonance of any material, the absorption may saturate as the intensity increases. This process is sketched out in Fig. 1.6 (a). It is expressed as,

$$\alpha(I) = \alpha_0 Is/(I + Is) \qquad (1.7)$$

where, I_s is the saturation intensity [32].

1.7 Reverse Saturable Absorption (RSA):

When a material absorbs light until the ground state is depleted of electrons and for a while transmission will be close to 1. Removal of light will make the dye relax back to its ground state. RSA can be observed in materials that absorb more in the excited state than in the ground state. As the intensity increases, the absorption increases and transmission decreases. Fig. 1.6 (b) explains the process in terms of three level model.

As the material absorbs light the first excited state, S_1, is populated. If σ_2 (exited state cross section) < σ_1 (ground state cross section) the material will be more transparent as the ground state is depleted of electrons. In other situation, $\sigma_2 > \sigma_1$ and absorption will increase as S_1 is populated [33].

1.8 Nonlinear refractive index:

In case of the nonlinear refractive index the phase of the light changes. Phase-matching is not required, so it may occur to some point in all materials. The nonlinearity in bulk materials, in a plane wave is not directly experiential as it is a pure phase change. Many geometry produce nonlinear effects from the nonlinear refractive index which consist of:

- Self-focusing or defocusing of a finite width beam
- Wave-mixing, two plane waves intersect at angles in a nonlinear medium, creating a phase-grating that can reflect (or deflect) light beams
- Formation of spatial solitons (stable propagating beams)
- Nonlinear interfaces
- Nonlinear waveguides etc.

The nonlinear refractive index is usually written as,

$$n(I) = n_o + n_2 I. \tag{1.8}$$

Where, the intensity of the light is I and n_2 is related to $\chi^{(3)}$ as nonlinear refractive index, which depends quadratically on the light's electric field, it changes the phase experienced by the light. It can be measured by interference with a reference beam using Kramers-Kronig relation. This relation tells us on how to relate the nonlinear refractive index to the spectrum of nonlinear absorption, assuming same level of excitation. It states that when optical intensity I is present at a frequency υ, a change in refractive index Δn can be determined by computing the change in absorption $\Delta\alpha$ at all possible frequencies υ′, in the same excitation conditions, and integrating with the following equation:

$$\Delta n(\nu) = \frac{c}{2\pi^2}\mathscr{P}\int_0^\infty \frac{\Delta\alpha(\nu')}{\nu'-\nu^2}\,d\nu' \,. \tag{1.9}$$

Where, $\mathscr{P}$ denotes the principal part of the integral. Because of the resonant denominator, the nonlinear refractive index due to nonlinear absorption may be quite large near a resonance.

1.8.1 Z-scan measurements of nonlinear refractive index

When an incident laser light has a Gaussian beam profile, the nonlinear medium will induce a lateral spatially varying refractive index. It grounds the beam to change its phase front with intensity if the refractive index increases. An intense light beam will tend to "self-focus" as it moves through the medium, here the nonlinear medium acts as a graded index lens. This lateral modification in beam shape because of the nonlinear refractive index inspired a new technique called the *z-scan*. It can measure both the sign and magnitude of the nonlinear refractive index and also the nonlinear absorption.

1.8.2 Mechanism of nonlinear refractive index

Ordinary Kerr effect illustrates a refractive index change that depends quadratically on applied electric field. The third-order nonlinearity generates a term that provides a nonlinear refractive index which is linear in the optical intensity and quadratic in the optical field, called the *optical Kerr effect* (OKE).

The classical portrait of a nonlinear refractive index is a nonlinear polarization, proportional to the polarizability of the medium governed by the electric field. We can express it physically as a simple harmonic oscillator; the oscillating charge separation initiated by the oscillating electric field. When the field is intense enough reaching the value of the internal fields inside the medium, the harmonic oscillator becomes nonlinear as the atomic cloud distorts. Through virtual mixing of the states of the atom or molecule the nonlinearities can be measured. These explanations offer hints as to which materials will be the most nonlinear [32, 34].

1.9 Organic Nonlinear Optical Chromophore:

In organic materials, NLO effects arise from the interaction between light and electrons inside individual molecular segments. Electrons are more accessible and give rise to faster and enhanced responses. The π electrons in organic structures with large delocalized π systems are affected by an external optical field, as they are relatively loosely bound to the nucleus. Also, the delocalized orbitals can be extended over the entire molecule giving large and fast polarization. Schematic diagram of electron delocalization in $\boldsymbol{D-\pi-A}$ system is shown in Fig. 1.7.

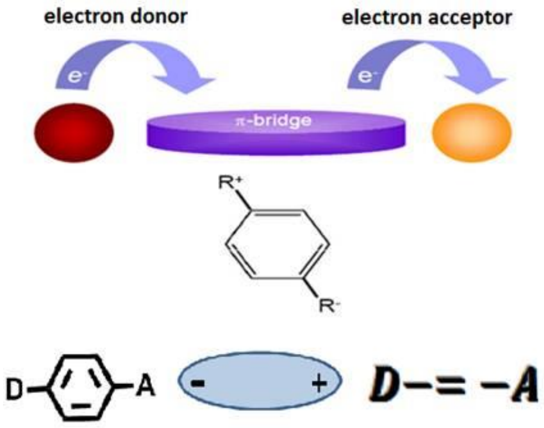


Figure 1.7: Schematic diagram of electron delocalization in D-π-A system.

So, a knob lies between the nonlinearity and the wavelength range of optical transparency. Functional groups can either donate (D) electron into the π system or accept (A) from it. To amplify the asymmetric electronic distribution in the ground state or the excited state configuration can be controlled with proper functional groups at the end of the π system. To exhibit second order effects, it is preferable for molecule to have a π electron system which delocalizes in response to an applied electric field such that the electron distribution results in spatial asymmetry. All even order effects vanishes in centrosymmetric systems, so charge asymmetry is essential for large second order processes. Third order NLO effects have a relationship between electronic structure and molecular geometry; mostly with the length of the π-system. Advantage of organic NLO materials lies in the opportunity of changing the structure to optimize their NLO properties. The conjugation length and the donor and acceptor group need to be tuned to achieve large molecular nonlinearity, while maintaining low absorption at operating wavelengths and longer stability [35-41].

1.10 Chalcone Derivatives:

Chalcones, precursors of flavonoids and isoflavonoids are 1, 3-diphenyl-2-propene-1-one, in which two aromatic rings are, linked with a three carbon α, β-unsaturated carbonyl system [42]. It was first isolated from Chinese liquorice (*Glycyrrhizin inflate*). Compounds with the backbone of chalcone possess various biological activities such as antimicrobial, anti-inflammatory, antiplatelet, antimalarial, anticancer, antileishmanial, antioxidant and antifungal have been reported. Chalcone also find several applications in agriculture; e.g., chalcone exhibit allelopathic activity, insecticides and fungicides [43-51].

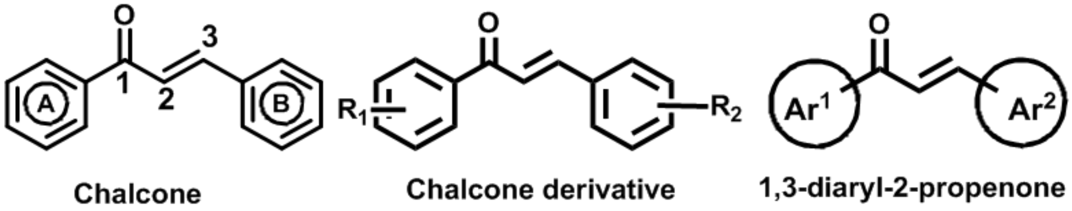


Figure 1.8: Structure and numbering system in chalcone (left), chalcone derivative (center) and 1,3-diaryl-2 propenone (right).

Due to its structural features the use of chalcone in material chemistry opens up a new field of research. Research works to explore the photo physical and material properties includes chalcone based liquid crystal materials and fluorescent materials. Substituted chalcones having donor and acceptor groups are excited due to extensive conjugation and internal charge transfer take place in it, which displays fluorescence property and sensor properties [52, 53].

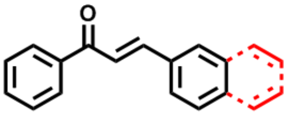
Despite of the several reports on the optical and other properties of some chalcone derivatives, investigation is necessary to tune those properties and explore their impending usefulness of NLO. In the parent structure of chalcone moiety, the presence of two aromatic rings and carbonyl group in between them provide unusual biological and material properties. Systematic modification of chalcone framework may sensibly bring enhanced and productive results in material chemistry as display and data storage, optical switching imaging, cancer therapy facilitated using multi photon absorption, optical power limiting, image manipulation, image processing etc. Motivated by the wide range of potential applicability of chalcone based materials the design, synthesis and studies of the material properties of some new chalcone derivatives are being taken up as the core objective of this research work.

1.11 Scope of this Thesis

The development of organic NLO materials for device applications is a multidisciplinary effort involving both theoretical and experimental studies in the fields of Chemistry, Physics, and Engineering. The main objectives of this thesis are:

- Design and synthesis of new compounds based on chalcone core unit which also includes functionalizing the α, β unsaturated carbonyl group. This –C=O moeity in chalcone plays the acceptor part, so it would be interesting to note the behavioural change related to this segment if it is replaced.
- Incorporation of heterocyclic units as a core in the main framework of chalcone.

- Integration of fused-ring moiety in the chalcone backbone.



- Characterisation of the newly synthesized chalcone to confirm their structure, purity, functional groups, conformation etc., using UV-Visible, IR, NMR and XRD techniques.
- Detailed study of their linear and nonlinear optical, fluorescence and electronic characteristics.

Mathematical detail is presented where it is utmost necessary for illustration, but generally a descriptive approach is favored. A rigorous and complete mathematical treatment of electromagnetic field theory, linear, and non-linear optics, is beyond the scope of this thesis.

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