CHAPTER 7

STUDIES ON LINEAR AND NONLINEAR OPTICAL PROPERTIES OF CYCLODODECANONE CRYSTALS

7.1. INTRODUCTION

The development of new materials with high third-order optical nonlinearities has been the focus of much recent research. The advantage of the three photon absorption of organic molecules at near infrared region is minimization of scattering losses and reduction of undesirable linear absorption in living organism (Boyd;2011) (Attas et al;2002). Excitation in the near infrared region is particularly attractive when pumping in the semi-transparent windows for biological media located at approximately 1100 nm to 1300 nm. Therefore, the radiation penetration depth through tissue can be maximized, facilitating tumour imaging and photo-annihilation in the absence of complicated and risky surgery. This unexplored field will have a broad impact in biology and medicine through three-photon induced photodynamic therapy in cancer treatment (Cohanoschi et al;2006) (Sai Santosh Kumar et al;2007).

This is the first investigation on nonlinear absorption and refractive index of cyclododecanone crystal family. The direct aldol condensation of benzaldehyde to cyclododecanone (CDD) reactions forms β-hydroxy carbonyl compounds and monobenzylidene cyclododecanone derivatives. The β-carbonyl compounds were stabilized by hydrogen bond interaction between the –OH group and –C=O groups. The monobenzylidene derivatives are due to less stable hydrogen bonds between –OH and –C=O groups, electrostatic interaction between aldehyde substituents and metal forms C–H O molecular interaction (Sathesh et al;2012).

In this chapter, the synthesized cyclododecanone derivatives and it is confirmed by proton and carbon NMR. The cyclododecanone derivative crystals were grown by slow evaporation method. Linear optical property of cyclododecanone crystals has studied using ultraviolet spectroscopy and optical constants such as extinction coefficient, optical conductivity and electrical conductivity are calculated theoretically as explained in Chapter 3. Refractive index of the crystals has studied using Abbe refractometer. Nonlinear absorption and nonlinear refractive index of cyclododecanone derivative has been studied by using Z-scan technique as explained in Chapter 4. The third harmonic generation crystals are of interest due to their attractive properties in the field of all optical switching. The material requirements for
all optical switch application, which have to be met are W>1 and T<1. So the material research is directed to application for all optical switching.

7.2. SYNTHESIS

**Figure 7.1**: Reaction scheme of cyclododecanone derivative

The stoichiometric ratio (1:1) of reactants cyclododecanone (CDD) (0.01M) and aromatic benzaldehydes (0.01M) were completely dissolved in methanol in the presence of sodium hydroxide as catalyst. The reaction scheme is shown in Fig.7.1. The mixture was stirred well for the direct aldol condensation reaction about 3 hours at room temperature 28°C, to synthesize the β-hydroxy carbonyl compounds and monobenzylidene cyclododecanone derivatives (Sathesh et al.;2012). The chemical structure of the synthesized compound was confirmed using $^1$H NMR and $^{13}$C NMR.

The direct aldol condensation of benzaldehyde to cyclododecanone (CDD) forms $\beta$ - hydroxy carbonyl compounds and monobenzylidene cyclododecanone derivatives. The formation of monobenzylidene derivatives were due to the less stable hydrogen bonds between –OH and –C=O groups, electrostatic interaction between aldehyde substituents and metal and the bulkiness of the benzaldehyde ring substituents. However, in case of aldehydes yielding benzylidene derivatives, the hydrogen of the –OH group is not available to form the hydrogen bond with the carbonyl group due to the strong interaction between the strong electron withdrawing halogen (Cl, Br) and the hydrogen of the –OH group. $\beta$-hydroxy carbonyl compounds also form the supramolecular helical motifs. The $\beta$-hydroxyl carbonyl derivatives form supramolecular helices via O–H O hydrogen bonds Sathish et al.
7.3. MECHANISM

![Mechanism Diagram]

Ketone reacts in presence of base NaOH, it observes the sodium and it reforms sodium enolate

The lone pair of electron shifts to double bond or alpha hydrogen. alpha hydrogen reacts with benzaldehyde of carbonyl carbon

Intermediate-1 will observed a proton from the water molecule and it forms cyclododecanone compound

Figure 7.2: Mechanism of cyclododecanone compound

7.4. NUCLEAR MAGNETIC RESONANCE

7.4.1. PROTON (1H) NMR

1H Nuclear magnetic resonance spectrum of cyclododecanone derivative has been recorded using chloroform as solvent on a Bruker spectra instrument opening at 400 MHz. The number of hydrogen in cyclododecanone derivative molecules are matching with hydrogen peaks at 1H NMR. The number of hydrogen in molecular structure of cyclododecanone compounds were confirmed by 1H nuclear magnetic resonance (NMR) spectral data.

a). 2-[Hydroxy (3-tolyl) methyl] cyclododecanone (3-CH$_3$ CDD)

1H NMR (400 MHz, CDCl$_3$): d=7.251–7.213 (t, J = 15.2 Hz, 1H, CHAr); 7.152 (s,1H, CHAr); 7.118– 7.099 (d, J = 7.6 Hz, 2H, CHAr); 4.775–4.743 (dd, J =9.2, 3.6 Hz, 1H, CH*(OH)); 2.978–2.923 (td, J = 4.1, 3.6 Hz, 1H, CH*-CHOH)
2.782–2.708 (qd, J = 8, 3.2 Hz, 1H, CHali); 2.611–2.604 (d, J = 2.8 Hz, 1H, CHali); 2.519–2.454 (qd, J = 8.4, 3.2 Hz, 1H, CHali); 2.356 (s, 3H, CAr–CH₃); 1.794–1.759 (m, 1H, OH); 1.698–1.670 (m, 1H, CHali); 1.550–1.490 (m, 1H, CHali); 1.307–1.117 (m, 15H, CHali).

b). 2-[Hydroxy (4-tolyl) methyl] cyclododecanone (4-CH₃ CDD)

¹H NMR (400 MHz, CDCl₃): δ = 7.253–7.212 (t, J = 15.2 Hz, 1H, CHAr); 7.155 (s, 1H, CHAr); 7.116–7.098 (d, J = 3.6 Hz, 1H, CH*(OH)); 2.964–2.916 (td, J = 3.6 Hz, 1H, CH*(OH)); 2.805–2.715 (qd, J = 9.6, 3.2 Hz, 1H, CHali); 2.558–2.547 (d, J = 4.4 Hz, 1H, CHali); 2.523–2.456 (qd, J = 6.7, 3.2 Hz, 1H, CHali); 1.836 (s, 3H, CH₃); 1.794–1.759 (m, 1H, OH); 1.698–1.670 (m, 1H, CHali); 1.552–1.477 (m, 1H, CHali); 1.346–1.165 (m, 15H, CH₂ali).

c). 2-(Hydroxy(4-methoxyphenyl)methyl) cyclododecanone (4-OMe CDD)

¹H NMR (400 MHz, CDCl₃): δ = 7.277–7.256 (s, 1H, CHAr); 6.902–6.880 (d, J = 3.6 Hz, 2H, CHAr); 4.803–4.772 (dd, J = 9.2, 3.2 Hz, 1H, CH*); 3.812 (s, 3H, OCH₃); 2.967–2.913 (td, J = 8.8, 3.2 Hz, 1H, CH₂ali); 2.873–2.842 (m, 2H, CH₂ali); 2.539–2.519 (t, J = 12 Hz, 2H, CH₂ali); 1.866 (bs, 2H, CH₂ali); 1.318 (s, 11H, CH₂ali); 1.245 (s, 1H, CHali); 1.132–1.107 (s, 15H, CH₂ali).

d). (E)-1-(2-Bromobenylidene) cyclododecanone (2-Br CDD)

¹H NMR (400 MHz, CDCl₃): δ = 7.635–7.615 (m, 1H, CHAr); 7.288–7.256 (s, 1H, CHvinylic); 7.344–7.168 (m, 3H, CHAr); 2.877–2.846 (m, 2H, CH₂ali); 2.539–2.509 (t, J = 12 Hz, 2H, CH₂ali); 1.893 (bs, 2H, CH₂ali); 1.318 (s, 11H, CH₂ali); 1.245 (s, 1H, CHali); 1.132–1.107 (t, J = 10 Hz, 2H, CH₂ali).

e). (E)-1-(2-Chlorobenylidene) cyclododecanone (2-Cl CDD)

¹H NMR (400 MHz, CDCl₃): δ = 7.464 (s, 1H, CHvinylic); 7.445–7.421 (td, J = 4.4, 1.2 Hz, 1H, CHAr); 7.288–7.256 (m, 3H, CHAr); 2.873–2.842 (m, 2H, CH₂ali); 2.549–2.519 (t, J = 12 Hz, 2H, CH₂ali); 1.866 (bs, 2H, CH₂ali); 1.318 (s, 11H, CH₂ali); 1.245 (s, 1H, CHali); 1.136–1.110 (t, J = 10 Hz, 2H, CH₂ali).

f). 2-[(4-Chlorophenyl) (hydroxy) methyl] cyclododecanone (4-Cl CDD)

¹H NMR (400 MHz, CDCl₃): δ = 7.434–7.338 (d, J = 2 Hz, 1H, CHAr); 7.327–7.311 (t, J = 4.4 Hz, 1H, CHAr); 7.286–7.280 (t, J = 2.4 Hz, 1H, CHAr); 7.267–7.262 (d, J = 2 Hz, 1H, CHAr); 4.835–4.802 (dd, J = 9.6, 4 Hz, 1H, CH*(OH)); 2.954–2.896 (td, J = 8.8, 4 Hz, 1H, CHali); 2.814–2.738 (q, J = 9.6, 3.2 Hz, 1H, CHali); 2.628–2.617 (d, J = 4.4 Hz, 1H, CHali); 2.425–2.353 (q, J = 8, 3.2 Hz, 1H, CHali); 1.892–1.825 (m, 1H, CHali); 1.606–1.571 (m, 1H, CHali); 1.531–1.473 (m, 1H, CHali); 1.392–1.160 (m, 15H, CHali).
g). 2-[(2-(Trifluoromethyl) phenyl) (hydroxy) methyl]cyclooctadecanone (2-CF₃ CDD)

1H NMR (400 MHz, CDCl₃): δ = 7.672–7.654 (d, J = 6.4 Hz, 2H, CHAr); 7.615–7.577 (t, J = 15.2 Hz, 1H, CHAr); 7.431–7.393 (t, J = 15.2 Hz, 1H, CHAr); 5.279–5.247 (dd, J = 8, 4.8, 1H, CH*(OH)); 3.080 (t, J = 12 Hz, 1H, CHali); 2.914–2.903 (d, J = 4.4 Hz, 1H, CHali); 2.620–2.558 (m, 2H, CHali); 1.720, (bs, 1H, OH, CH2ali), 1.308–1.129 (m, 15H, CHali).

h). 2-[Hydroxy (phenyl) methyl] cyclododecanone (Benz-CDD)

1H NMR (400 MHz, CDCl₃): δ = 7.385–7.258 (m, 5H, CHAr); 4.823–4.783 (dd, J = 8, 3.2 Hz, 1H, CH*(OH)); 2.953–2.897 (td, J = 8.8, 4 Hz, 1H, CHAli); 2.804–2.728 (qd, J = 9.6, 3.2 Hz, 1H, CHAli); 2.628–2.617 (d, J = 4.4 Hz, 1H, CHAli); 2.425–2.353 (qd, J = 8, 3.2 Hz, 1H, CHAli); 1.892–1.825 (m, 1H, CHAli); 1.606–1.571 (m, 1H, CHAli); 1.531–1.473 (m, 1H, CHAli); 1.392–1.160 (m, 15H, CHAli).

7.4.2. CARBON (13C) NMR

13C Nuclear magnetic resonance spectrum of cyclooctadecanone derivative has been recorded using chloroform as solvent on a Bruker spectra instrument opening at 400 MHz. The number of carbon in cyclooctadecanone derivative molecules are matching with carbon peaks at 13C NMR. The number of carbon in molecular structure of cyclooctadecanone compounds were confirmed by 13C nuclear magnetic resonance (NMR) spectral data.

a). 2-[Hydroxy (3-toly] methyl] cyclooctadecanone (3-CH₃ CDD)

13C NMR (100 MHz, CDCl₃): δ = 215.0, 142.1, 138.2, 128.8, 128.4, 127.3, 123.8, 75.3, 59.2, 39.2, 27.3, 26.4, 26.0, 24.2, 23.8, 23.7, 22.8, 22.3, 21.6.

b). 2-[Hydroxy (4-toly] methyl] cyclooctadecanone (4-CH₃ CDD)

13C NMR (100 MHz, CDCl₃): δ = 214.8, 139.1, 137.6, 129.1, 126.5, 75.1, 59.2, 39.2, 27.3, 26.3, 25.9, 24.2, 23.8, 23.7, 22.8, 22.3, 21.5, 21.0.

c). 2-(Hydroxy(4-methoxyphenyl)methyl) cyclooctadecanone (4-OMe CDD)

13C NMR (100 MHz, CDCl₃): δ = 215, 159.40, 134.27, 127.88, 113.98, 77.35, 77.03, 76.71, 74.88, 59.36, 55.30, 39.25, 30.94, 27.34, 26.43, 26.02, 24.25, 23.82, 23.71, 22.73, 22.36, 21.63.

d). (E)-1-(2-Bromobenzenylidene) cyclooctadecanone (2-Br CDD)

13C NMR (100 MHz, CDCl₃): δ = 205.1, 142.8, 138.0, 136.5, 132.6, 130.5, 129.3, 127.1, 124.0, 38.8, 26.5, 26.5, 25.4, 24.4, 24.2, 24.1, 24.0, 23.1, 22.5.
e). (E)-1-(2-Chlorobenzyldiene) cyclododecanone (2-Cl CDD)

$^{13}\text{C}$ NMR (100 MHz, CDCl$_3$): $d = 205.0, 143.2, 136.0, 134.7, 133.8, 130.3, 129.4, 129.2, 126.4, 38.8, 26.5, 26.4, 25.4, 24.4, 24.2, 24.1, 23.9, 23.1, 22.5.

f). 2-[(4-Chlorophenyl) (hydroxy) methyl] cyclododecanone (4-Cl CDD)

$^{13}\text{C}$ NMR (100 MHz, CDCl$_3$): $d = 214.7, 140.6, 133.7, 128.7, 128.0, 74.4, 58.9, 39.7, 27.3, 26.4, 25.9, 24.2, 23.8, 23.7, 22.6, 22.4, 21.5.

g). 2-[(2-(Trifluoromethyl) phenyl) (hydroxy) methyl] cyclododecanone (2-CF$_3$ CDD)

$^{13}\text{C}$ NMR (100 MHz, CDCl$_3$): $d = 214.7, 141.1, 132.5, 128.0, 127.9, 125.7, 125.7, 70.4, 58.7, 39.2, 27.6, 26.3, 25.8, 24.3, 24.0, 23.9, 23.5, 22.4, 21.6.

h). 2-[(Hydroxy (phenyl) methyl] cyclododecanone (Benz-CDD)

$^{13}\text{C}$ NMR (100 MHz, CDCl$_3$): $d = 214.9, 142.1, 128.5, 128.0, 126.6, 75.3, 59.1, 39.5, 27.3, 26.3, 25.9, 24.2, 23.8, 23.8, 22.8, 22.3, 21.5;

7.5. CRYSTAL GROWTH

Single crystals of CDD derivative were grown in mixture of solvent tetrahydrofuran (THF) and ethanol (1:1). The solution was filtered using filter paper and allowed to evaporate slowly at room temperature. The purity of synthesized compound was improved by successive recrystallization process and filtration. The crystals were grown in the period of 3-4 days as shown in Fig. 7.3.
Cyclododecanone derivative crystals were subjected to spectral analysis to study their linear optical properties. The absorption spectrum of cyclododecanone crystals has been recorded in the range of 190-1100nm using ELICO SL 218 double beam Ultraviolet spectrophotometer. The absorption spectrum of cyclododecanone derivative crystals shows the lower cutoff wavelength at 310 nm (approx.) onwards. Cyclododecanone derivative crystals have found to be wide transparency in the region of 310-1100nm.

The absorption spectrums of cyclododecanone derivative crystals are shown in Fig. 7.4. The absorption edge of cyclododecanone is 307nm, when it is bonding with benzaldehyde shifts the absorption edge to 314nm. Benzaldehyde with CDD has increases the cut-off wavelength of 7nm and increases the absorption of 2.719a.u. Similarly the presence of -CH₃ (methyl) group in meta and para position of benzaldehyde shifts the cut-off wavelength of 2nm to 4nm respectively. -4CH₃ is increases the absorption of 2.0987a.u and as well as -3CH₃ decreases the absorption to 0.4389a.u. The change of position of methyl group in benzaldehyde varies the cut-off wavelength of 2nm and absorption of 1.659a.u. The optical response of the molecule depends on the linearity of molecule and molecular packing. From the discussion, -3CH₃ group has low absorption and low cutoff compare to -4CH₃. 3-methyl benzaldehyde and 4-methyl benzaldehyde shifts the absorption edge of 9nm.
and 11nm and the absorption coefficient 1.843a.u and 3.503a.u respectively, when compared with cyclododecanone crystal.

4-methoxy benzaldehyde and 4-methyl benzaldehyde were in para position of benzene ring, differentiate from the presence of oxygen. When compare to the CDD-Benz, the shift of cut-off wavelength of 4-methoxy and 4-methyl is 11nm and 17nm respectively. The presence of oxygen (–OCH₃) in aldehyde shifts the cut-off wavelength of 6nm from the absorption edge of -4CH₃CDD. When compared to the absorption of CDD-Benz, 4-methyl and 4-methoxy is increases of 3.4023a.u and 5.0543a.u respectively. Similarly the oxygen in methoxy group increases the absorption of 1.652a.u with respect to 4-methyl (-4CH₃).

The absorption edge of 2-chloro and 2-bromo benzaldehyde is 371nm and 376nm respectively. The absorption edge of -2cl and -2br shifts 57nm and 62nm respectively, when compared to CDD-Benz. The absorption coefficient of 2-Cl and 2-Br is coming around 4.4341a.u and 1.4148a.u respectively. Due to the presence of 2-Cl and 2-Br increases the absorption 5.8384a.u and 2.8198a.u respectively.

As explained in Chapter.3, The optical constant such as absorption coefficient, energy band gap (Tauc’s method), extinction coefficient, optical conductivity and electrical conductivity were calculated. The band gap value of cyclododecanone crystals could be used in optical devices like optical switching and optical attenuators. The large band gap of the cyclododecanone crystals confirms the large transmittance in the visible region. Molecule should have to choose a large band gap for telecommunication, i.e., \( E_g > 1.65 \text{ eV} \) reported by Haque et.al;2010. Cyclododecanone derivative has large band gap, and it is suitable for optical communication. The high value of optical conductivity \( 10^{12} \text{ s}^{-1} \) shows the very good optical or photo response of the material. The calculated optical constants are given in Table.7.1.

The refractive index measurements of CDD derivative single crystals were measured using Abbe refractometer connected by digital thermometer. Each sample independently contact with the central prism and the contact liquid (Monobromo naphthalene), which makes the sample close contact to the prism. Open the secondary
prism completely and stand a milky white reflector against the opposite side of secondary prism so that external light (sodium lamp) reflects on the reflector and it horizontally penetrates the sample. While observing to the eyepiece, gently turn the measurement knob to set the scale indication approximately to the refractive index shown on the test piece. The refractive index measured at ambient temperature for CDD derivative crystals were measured and it is shown in Table.7.1.

Table.7.1. Optical parameters of cyclododecanone derivative crystals

<table>
<thead>
<tr>
<th>Compound name</th>
<th>UV Cut-off wavelength (nm)</th>
<th>Extinction coefficient (190-1100nm)</th>
<th>Optical Conductivity (per second)</th>
<th>Band gap (eV)</th>
<th>Refractive index (Abbe refractometer)</th>
<th>Electrical conductivity (Ohm/m)</th>
<th>Thickness of crystal (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Br CDD</td>
<td>376</td>
<td>10⁻³</td>
<td>10¹¹</td>
<td>3.2895</td>
<td>1.639 (28.6°C)</td>
<td>10³</td>
<td>1.13</td>
</tr>
<tr>
<td>2-Cl CDD</td>
<td>371</td>
<td>10⁻³</td>
<td>10¹²</td>
<td>3.1653</td>
<td>1.642 (29.2°C)</td>
<td>10³</td>
<td>0.44</td>
</tr>
<tr>
<td>4-Cl CDD</td>
<td>324</td>
<td>10⁻³</td>
<td>10¹²</td>
<td>3.8294</td>
<td>1.621 (29.2°C)</td>
<td>10³</td>
<td>0.48</td>
</tr>
<tr>
<td>4-OMe CDD</td>
<td>324</td>
<td>10⁻³</td>
<td>10¹²</td>
<td>3.7802</td>
<td>1.643 (28.9°C)</td>
<td>10³</td>
<td>0.76</td>
</tr>
<tr>
<td>3-CH₃ CDD</td>
<td>316</td>
<td>10⁻⁴</td>
<td>10¹²</td>
<td>3.9123</td>
<td>1.626 (28.7°C)</td>
<td>10³</td>
<td>1.28</td>
</tr>
<tr>
<td>4-CH₃ CDD</td>
<td>318</td>
<td>10⁻³</td>
<td>10¹¹</td>
<td>3.8603</td>
<td>1.637 (29.1°C)</td>
<td>10³</td>
<td>0.97</td>
</tr>
<tr>
<td>2-CF₃ CDD</td>
<td>314</td>
<td>10⁻³</td>
<td>10¹²</td>
<td>3.9276</td>
<td>1.609 (28.1°C)</td>
<td>10³</td>
<td>0.62</td>
</tr>
<tr>
<td>Benz-CDD</td>
<td>314</td>
<td>10⁻³</td>
<td>10¹²</td>
<td>3.8955</td>
<td>1.602 (25.4°C)</td>
<td>10³</td>
<td>1.00</td>
</tr>
<tr>
<td>CDD</td>
<td>310</td>
<td>10⁻⁴</td>
<td>10¹²</td>
<td>3.9939</td>
<td>1.548 (25.4°C)</td>
<td>10³</td>
<td>0.50</td>
</tr>
</tbody>
</table>

7.7. NONLINEAR OPTICAL PROPERTY

Nonlinear refractive index and nonlinear absorption of cyclododecanone derivatives crystals were calculated using Z-scan technique. The optical absorption of sample at focal length changes the refractive index of the material. The change of refractive index affects the transmittance of the sample. A valley (minimum transmittance) followed by peak (maximum transmittance) is a negative refractive index. CDD derivative crystals show the self-defocussing effect as shown in Fig. 7.5.
Figure 7.5: Nonlinear refractive index of cyclododecanone derivatives

As explained in Chapter 4, the nonlinear refractive index and absorption has been calculated for cyclododecanone crystal derivative. The linear transmittance (S) of the CDD crystals varies from 1mm-3mm. The absorption of the CDD derivatives is measured from UV-Vis-NIR spectrophotometer. The linear refractive has been measured from Abbe's refractometer. The nonlinear change in refractive index of cyclododecanone crystal is coming around 1.2253. NLRI has increased of 1.7952, when cyclododecanone is bonding with benzaldehyde. It is observed that the decreases of nonlinear refractive in 3-CH$_3$CDD and 4-CH$_3$CDD, 0.9625 and 0.5983 respectively. The presence of -2BrCDD, -2ClCDD, -4ClCDD, and -2CF$_3$CDD are increasing the nonlinear refractive 1.2455, 1.4309, 0.9685 and 1.2963 respectively, when compared to the CDD crystal. In the crystal 4-CH$_3$CDD and 4-OMeCDD has nonlinear change of 0.5983 and 1.1089, the presence of oxygen in the para position of benzaldehyde is increases the nonlinear refractive index.

The nonlinear refractive index of -2CICDD and -4CICDD is 1.4309 and 0.9685 respectively. The change in position of chlorine in ortho to para position of benzaldehyde, decreases the change in nonlinear refractive index has been observed. Similarly the nonlinear refractive index of -3CH$_3$CDD and -4CH$_3$CDD is 0.9685 and 0.5983 respectively. The change in position of methyl in meta to para position, decreases the nonlinear refractive index has been observed. The linear molecule is
decreasing the change in nonlinear refractive index and it is suitable for optical communication. The real part of third order nonlinear susceptibility is proportional to nonlinear refractive index \((n_2)\). The nonlinear refractive index has been calculated and it is given in Table 7.2.

![Figure 7.6: Nonlinear absorption of cyclododecanone derivatives](image)

Nonlinear absorption extracts from the open aperture method. The saturation absorption or maximum transmittance enhances the peak and suppresses the valley at the focal point. The normalized transmittance \((S=1)\) of the open aperture shows enhanced transmission at the focus, which means saturation of absorption at high intensity. CDD derivative crystals are producing the saturation absorption, and it is shown in Fig. 7.6.

It is clearly observed that the crystal CDD, CDD-Ben and 2-Br has lowest nonlinear absorption. The crystals 4-OMeCDD, 2Cl-CDD and 2CF3-CDD has second lowest nonlinear absorption as shown in characteristic peak. Among these crystals 3-CH3-CDD, 4-CH3-CDD and 4Cl-CDD has high nonlinear absorption. But all the cyclododecanone derivative crystal has lowest nonlinear absorption and it is suitable for application. The imaginary part of third order nonlinear susceptibility is proportional to nonlinear absorption \((\beta)\). The nonlinear absorption has been calculated and it is given in Table 7.2.
The calculated value of the nonlinear refractive index ($n_2$) and the nonlinear absorption ($\beta$) of CDD derivative crystals are shown in Table.7.2. The mechanism of nonlinear response of crystal is due to the thermal nonlinear optical effects. The origin of thermal nonlinearity is that some fraction of the incident laser power is absorbed in passing through an optical material. The temperature of the illuminated portion of the material consequently increases, which leads to a change in the refractive index of material. The refractive index can either decrease or increase with changes in temperature, depending on the internal structure of a material. Thermal effects are usually the dominant nonlinear optical mechanism for continuous wave laser beams. The nonlinear polarization is depending on the applied field strength. In the same manner mechanism can be explained in terms of nonlinear susceptibility or nonlinear refractive index. The characteristic time scale for nonlinear response of material from the typical value based on $n_2$ (10^{-11} cm²/w) or $\chi^3$ is developed by Robert Boyd. As per the characteristic time scale CDD derivative crystals are possibly response in microseconds (10^{-3}) time for optical switching devices.

Table.7.2. Nonlinear absorption, refractive index and third order susceptibility of cyclododecanone derivative

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\beta$ (m/W)</th>
<th>$n_2$ (m²/W)</th>
<th>$\chi^3$ (esu)</th>
<th>W (&gt;1)</th>
<th>T (&lt;1)</th>
<th>Re($\chi^3$)/Im($\chi^3$)</th>
<th>SHG</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDD</td>
<td>5.97x10^{-5}</td>
<td>2.08x10^{-11}</td>
<td>1.279x10^{-7}</td>
<td>38.9</td>
<td>1.81</td>
<td>6.92</td>
<td>Nil</td>
</tr>
<tr>
<td>Benz-CDD</td>
<td>6.14 x10^{-8}</td>
<td>3.68 x10^{-11}</td>
<td>2.402 x10^{-7}</td>
<td>86.5</td>
<td>1.06</td>
<td>11.88</td>
<td>Nil</td>
</tr>
<tr>
<td>3CH3 CDD</td>
<td>2.47x10^{-4}</td>
<td>1.88x10^{-11}</td>
<td>1.515 x10^{-3}</td>
<td>10.4</td>
<td>8.30</td>
<td>1.51</td>
<td>Nil</td>
</tr>
<tr>
<td>4CH3 CDD</td>
<td>1.64x10^{-4}</td>
<td>9.44 x10^{-12}</td>
<td>8.535 x10^{-9}</td>
<td>15.8</td>
<td>11.0</td>
<td>1.14</td>
<td>SHG</td>
</tr>
<tr>
<td>4-OMe CDD</td>
<td>1.17x10^{-4}</td>
<td>2.24 x10^{-11}</td>
<td>1.584 x10^{-9}</td>
<td>22.9</td>
<td>3.3</td>
<td>3.80</td>
<td>Nil</td>
</tr>
<tr>
<td>2-CF3 CDD</td>
<td>9.82x10^{-4}</td>
<td>2.52 x10^{-11}</td>
<td>1.684 x10^{-9}</td>
<td>41.3</td>
<td>2.47</td>
<td>5.08</td>
<td>Nil</td>
</tr>
<tr>
<td>2Br- CDD</td>
<td>6.63x10^{-4}</td>
<td>2.96 x10^{-11}</td>
<td>2.027 x10^{-9}</td>
<td>21.4</td>
<td>0.6</td>
<td>8.84</td>
<td>Nil</td>
</tr>
<tr>
<td>2Cl- CDD</td>
<td>3.75x10^{-4}</td>
<td>7.85 x10^{-11}</td>
<td>5.304 x10^{-9}</td>
<td>52.5</td>
<td>1.81</td>
<td>6.94</td>
<td>Nil</td>
</tr>
<tr>
<td>4Cl- CDD</td>
<td>3.19x10^{-4}</td>
<td>3.19 x10^{-11}</td>
<td>2.143 x10^{-9}</td>
<td>15.8</td>
<td>7.26</td>
<td>1.73</td>
<td>Nil</td>
</tr>
</tbody>
</table>

The nonlinear refractive index of materials depends on the intensity of applied laser beam Haque et.al. The high speed (<100 ps) of optical switching offers the possibility of dramatic increases in the speed and efficiency of a variety of applications. The
increase in intensity of laser possibly to achieve nano to picoseconds optical response in cyclododecanone compounds. Two figures of merit, W and T, have been calculated to be $W=n_2 I/\omega \lambda (>1)$ and $T= \beta \lambda/n_2<1$, respectively. All the results show that CDD crystals have potential materials for all-optical switching. There is requirement of high ratio of real and imaginary nonlinear susceptibility for all optical switching application (AOS). CDD derivative crystals have high ratio of susceptibility, implies that the crystals are suitable for IR switching application.

7.8. CONCLUSION

Cyclododecanone derivative crystals are a significant and promising candidate for photonic application. Cyclododecanone (CDD) and its derivatives have been synthesized by direct aldol condensation reaction. CDD derivative crystals were grown in the mixture of solvent tetrahydrofuran and ethanol by slow evaporation method. The spectroscopic characterization of carbon NMR and proton NMR has been investigated. The linear optical property of cyclododecanone derivative crystals has been studied using UV-VIS-NIR spectroscopy. Cyclododecanone crystals have found to be wide transparency in the region of 310-1100nm and the various constant such as optical band gap ($E_g$), extinction coefficient (K) and optical conductivity ($\sigma_0$) were calculated theoretically. The high value of optical conductivity ($10^{12} \text{s}^{-1}$) shows the very good optical or photo response of the material and it is favorable for optical communication devices. Z-scan study reveals the self-defocusing effect and saturation absorption of cyclododecanone crystals. The third order NLO susceptibility ($\chi^3$) of crystal is $10^{-5}$ to $10^{-6}$ esu, nonlinear refractive index ($n_2$) is $10^{-11} \text{ m}^2/\text{W}$ and nonlinear absorption ($\beta$) is $10^{-4}$ to $10^{-5}$ m/W, has been studied using Z-scan technique using He-Ne laser.