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Study of Nonlinear Optical Properties of Nematic Liquid Crystal Material by Z-Scan Technique

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ABSTRACT

The nonlinear optical properties of nematic liquid crystal material have been studied at different concentrations using Z-Scan technique. Experiments are performed using continuous wave (CW) diode solid state laser at 473 nm wavelength and 20 mW power. The nonlinear absorption coefficient β is calculated using open aperture Z-Scan data, while its nonlinear refractive index n_2 is measured using the closed aperture Z-Scan data. In this work, six concentrations were prepared for (Di-Cinnamylidene Benzidine), these concentrations were (9×10^{-5}, 8×10^{-5}, 7×10^{-5}, 6×10^{-5}, 5×10^{-5} and 4×10^{-5})M. The optical absorption and transmission spectra for these concentrations were measured by using UV-VIS spectrophotometer. Our results show that the nonlinearity are changed significantly with concentrations, in addition, the optical limiting behavior has been studied. The results confirmed the capability of the sample to be used as optical limiter device.

***Keywords*:** Nematic liquid crystal; Z-Scan technique; nonlinear refractive index; optical limiting

1. INTRODUCTION

Research on liquid crystal has been involved in chemistry, physics, biology, electric and electronic engineering and many other fields. Most of these researches have been reported by the universities and research institutions. The study of liquid crystals began in 1888 by an

Australian botanist F. Reinitzer [1,2]. Liquid crystal materials are unique in their properties and usages.

As research into this field continues and as new applications are developed, liquid crystals will play an important role in modern technology, it can be promising materials for optical switching and optical power limiting applications [3]. In the nematic phase the rod shaped molecules are oriented on the average along an axis called the director. The nematic phase has long range orientational order [4,5].

M. Sheik-Bahae *et al*. reported the Z-Scan technique for measuring both the nonlinear refractive index and nonlinear absorption coeffiecint for a wide varity of materials. Z-Scan method provides a straight forward method for the determination of the nonlinear refractive index and the nonlinear absorption coefficient. The simplicity of both the experimental set-up and the data analysis has allowed the technique to become widely used by research groups [6].

A. Rodríguez *et al*. study the nonlinear refractive index response of several organic dyes and their impact on the nonlinear optical properties (NLO) of nematic liquid crystals (LC) was performed via Z-Scan measurements, a low power (CW) He-Ne laser system ($\lambda \approx 633$ nm) was implemented. Studies were carried out at the low absorption spectroscopic region of the implemented samples (dyes, liquid crystals and mixtures at different ratios of these materials). The implemented dyes have shown the largest optical nonlinearities and represent the main contributors to the cubic NLO-properties of the LC: Dye mixtures [7].

Z. Xiaoqiang *et al*. study the nonlinear optical properties of a series of azobenzene liquid-crystalline materials, which have different side-chain lengths in their molecular structure from one to another, were investigated using Z-Scan method under picosecond pulse laser at (CW) wavelengths (488, 532 and 1064) nm.

The mechanism accounting for the process of nonlinear refraction was discussed under different laser excitations. The polymer films possess very large nonlinear refraction at all the three different laser excitations [8]. Z. Fryad *et al.* study the investigation of the nonlinear refractive index and nonlinear absorption coefficientof {(1Z)(Dimethylamino)phenyl] methylene} 4-nitrobenzocarboxyhydrazone mono-hydrate (DMPM4NBCHM) solution using Z-Scan technique with a (CW) Argon ion laser. The results show that this type of organic material has a large nonlinear absorption and nonlinear refractive index at 488 nm and 514 nm [9]. The aim of this work was the use of the Z-Scan technique to study the nonlinear optical properties of (Di-Cinnamylidene Benzidine) at different concentrations with (CW) diode solid state laser at 473 nm wavelength and 20 mW power. Also preparing a good limiter device for many applications.

2. THEORY

There is considerable interest in finding materials having fast nonlinearities. This interest, that is driven primarily by the search for materials for all-optical switching and sensor protection applications, concerns both nonlinear absorption (NLA) and nonlinear refraction (NLR). The absorption of the material at high intensity is given by [10,11]:

$$\alpha = \alpha_o + \beta I \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where I is the incident intensity, α_o is the linear absorption coefficient and β is the nonlinear absorption coefficient related to the intensity. At high intensity, the refractive index is given by:

$$n = n_o + n_2 I \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where n_o is the linear refractive index , and n_2 is the nonlinear refractive coefficient. The nonlinear optical properties can be investigated by Z-Scan technique at which it can be used to determine the nonlinear refractive index when closed-aperture geometry is used, and nonlinear absorption coefficient with open aperture. The nonlinear refractive coefficient is calculated from the peak to valley difference of the normalized transmittance by the following formula [10]:

$$\mathrm{n}_2 = \frac{\Delta\Phi_o}{I_o L_{eff} K} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where, $K = 2\pi/\lambda$, λ is the beam wavelength, I_o is the intensity at the focal spot ,$\Delta\Phi_o$ is the nonlinear phase shift,

$$\Delta\mathrm{T}_{p-v} = 0.406|\Delta\Phi_o| \ldots\ldots\ldots\ldots(4)$$

$\Delta\mathrm{T}_{p-v}$ the difference between the normalized peak and valley transmittances,
L_{eff} is the effective length of the sample, determined from [10]:

$$\mathrm{L}_{eff} = \frac{(1 - exp^{-\alpha_o L})}{\alpha_o} \ldots\ldots\ldots\ldots(5)$$

where L is the sample length, α_o is given as [11]:

$$\alpha_o = \frac{\ln(\frac{1}{T})}{t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

where (t) is the thickness of sample and T is the transmittance n_o obtained from equation [11]:

$$\mathrm{n}_o = \frac{1}{T} + \left[\left(\frac{1}{T^2} - 1\right)\right]^{1/2} \ldots\ldots\ldots(7)$$

The intensity at the focal spot is given by [11]:

$$\mathrm{I}_o = \frac{2P_{peak}}{\pi\omega_o{}^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Is defined as the peak intensity within the sample at the focus, where ω_o is the beam radius at the focal point, the coefficients of nonlinear absorption (β), can be easily calculated by using following equation [11]:

$$\beta = \frac{2\sqrt{2}\,T(z)}{I_o L_{eff}} \ldots\ldots\ldots\ldots \quad \ldots\ldots \quad ..(9)$$

where T(z): The minimum value of normalized transmittance at the focal point, where (z = 0) Fig. (1) illustrates a peak and valley as the sample is translated [12].

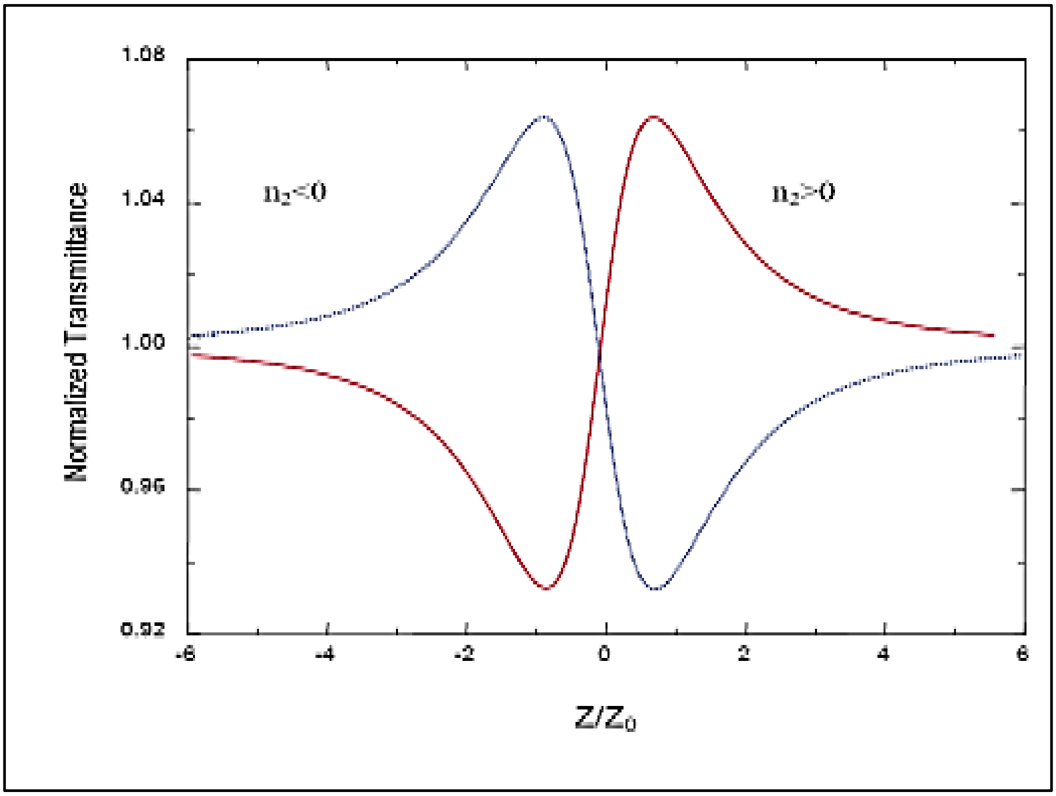

Fig. 1. Simulated closed-aperture Z-Scan signature for a sample with positive and negative nonlinear refractive coefficient [12].

It is a material with a negative nonlinear refractive index and a thickness smaller than the diffraction length of the focused beam (a thin medium). This can be regarded as a thin lens of variable focal length. Starting the scan from a distance far away from the focus (negative z), the beam fluence is low and negligible nonlinear refraction occurs; hence, the transmittance in Fig. (1) remains relatively constant. As the sample is brought closer to focus, the beam irradiance increased leading to self-focusing in the sample.A negative self-focusing prior to focus will tend to collimate the beam, causing a beam narrowing at the aperture which results in the increase of the measured transmittance. As the scan in z continues and the sample passes the focal plane to the right (positive z), the same self-defocusing increases the beam divergence, leading to beam broadening at the aperture, and thus to a decrease of transmittance. This suggests that there is a null as the sample crosses the focal plane. This is analogous to placing a thin lens at or near the focus, resulting in a minimal change of the far-field pattern of the beam.

The Z-Scan is completed as the sample is moved away from focus (positive z) so that the transmittance becomes linear since the fluence is again low. A prefocal transmittance maximum (peak) followed by a post focal transmittance minimum (valley) is, therefore, the Z-Scan signature of a negative refractive nonlinearity. Positive nonlinear refraction, following the same analogy, gives rise to an opposite valley-peak configuration [12].

3. EXPERIMENTAL WORK

Preparation of Di-Cinnamylidene Benzidine will be explain in detail in the following paragraph:

3. 1. Material Preparation

Di-cinnamylidene benzidine was prepared by mixing (1.84 g; 0.01 mol) of benzidine dissolved in (10 mL) of absolute ethanol with (2.64 g; 0.02 mol) of cinnamaldehyde dissolved in (10 mL) of absolute ethanol, then three drops of glacial acetic acid were added to the prepared mixture and left under reflux for (2) hours, producing yellowish solid product. The solid product formed was separated by filtration, purified by recrystallization from ethanol, washed with ethanol, and then dried. Figure (2) show preparation of Di-cinnamylidene benzidine.

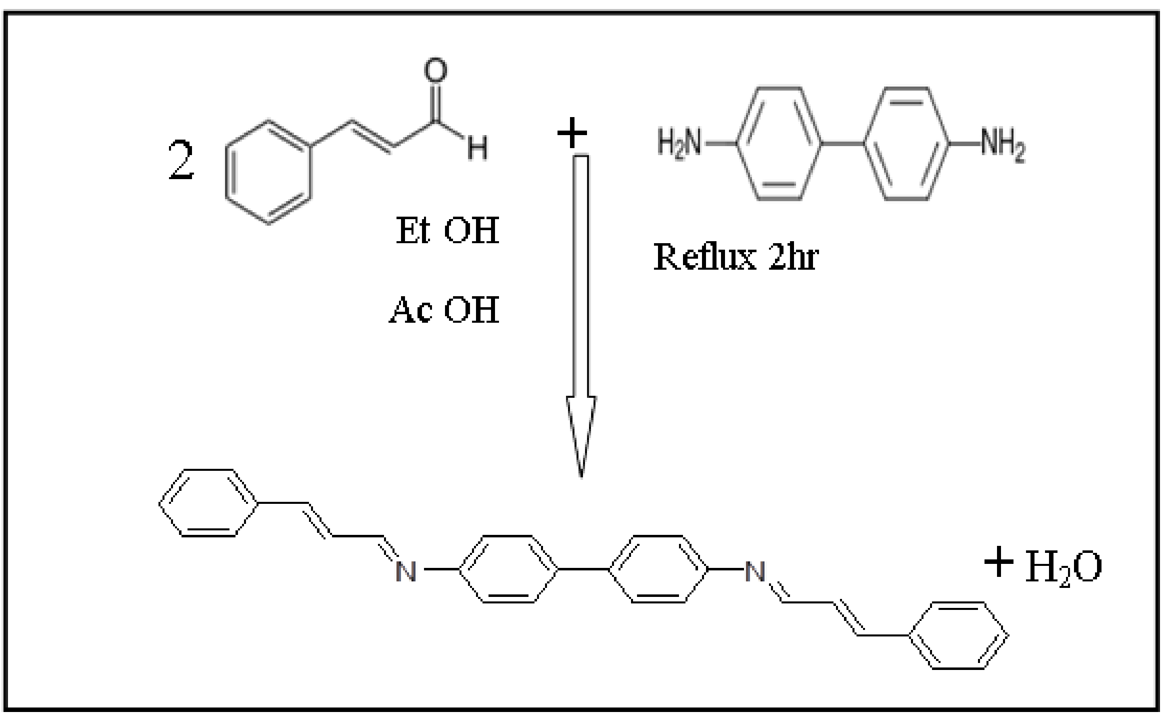

Fig. 2. Preparation design of Di-cinnamylidene benzidine.

Solutions of concentrations ($1x10^{-3}$ M) for (Di-Cinnamylidene Benzidine), in ethanol solvent were prepared. The powder was weighed by using an electronic balance type (BL 210 S), Germany, having a sensitivity of four digits. Different concentrations were prepared according to the following equation:

$$W = \frac{M_W \times V \times C}{1000} \dots\dots\dots\dots\dots\dots\dots \;..(10)$$

where, W: Weight of the dissolved in material (g), M_w: Molecular weight of the material (g /mol),V: Volume of the solvent (mL), C: The concentration (M).

The prepared solutions were diluted according to the following equation:

$$C_1V_1 = C_2V_2 \dots\dots\dots\dots\dots\dots\dots..(11)$$

where:
C_1: Primary concentration;
C_2: New concentration;
V_1: The volume before dilution;
V_2: The volume after dilution.

In this work ,six concentrations were prepared for (Di-Cinnamylidene Benzidine), the concentrations were (9×10^{-5}, 8×10^{-5}, 7×10^{-5}, 6×10^{-5}, $5\times10^{-5}$and 4×10^{-5}) M.

3. 2. Absorption And Transmission Spectra

The linear absorption and transmission spectra of (Di-Cinnamylidene Benzidine) at different concentrations recorded for wavelengths (190 to 900) nm were tested using UV-VIS spectrophotometer model (Aquarius 7000, Optima , Japan), at room temperature, as shown in Figures (3) and (4). The absorption spectra show two clear bands, the first at wavelength (290) nm, is due to the phenomena of positional excitation for the benzene rings because the absorption happened for the (C=C) group of the aromatic system and azomethane (C=N) group, that resulted from an electronic transitions for ($\pi\rightarrow\pi^*$).

The electronic transitions between azomethane groups and aromatic rings (Phenyl-N) and (Phenyl-C). The second band between (340-400) nm with highest wavelengths belongs to transition of ($n\rightarrow\pi^*$) that referred to the neighboured active azomethine groups, which acted as an electron-receptor where the free lone pair of electron was available at each nitrogen atom (has ability for sharing at resonance phenomena). The present results show that the absorption peaks for (Di-Cinnamylidene Benzidine) of different concentrations of in ethanol solvent were shifted toward the longer wavelengths with decreasing concentrations.

This shift obtain due to decreasing number of molecules per volume unit at low concentrations, we show absorption increasing with increases concentration. The optical transmission of (Di-Cinnamylidene Benzidine) are shown a variable behavior of the transmission as a function of the incident wavelength.

The linear refractive coefficient (n_o) and linear absorption coefficient (α_o) of (Di-Cinnamylidene Benzidine), obtained from equations (6,7) respectively [9]. The values of (α_o) and (n_o) are decreased with decreasing the concentrations of solutions as listed in Table (1) .

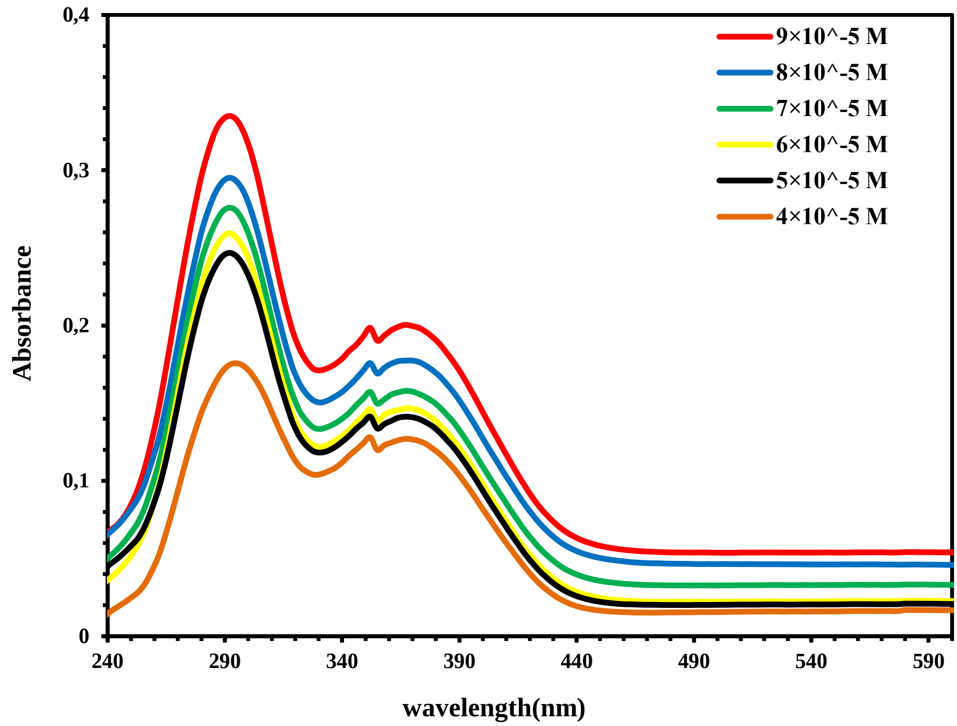

Fig. 3. Absorption spectra of (Di-Cinnamylidene Benzidine) in ethanol solvent at different concentrations.

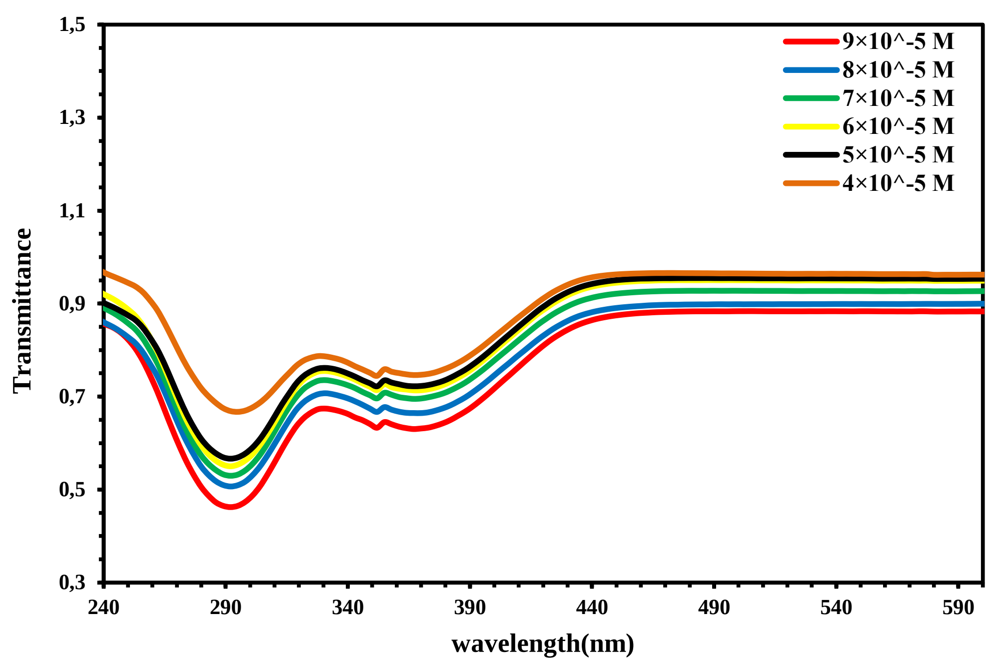

Fig. 4. Transmission spectra of (Di-Cinnamylidene Benzidine) in ethanol solvent at different concentrations.

4. RESULT AND DISCUSSION

The Z-scan experiments will be explain in detail in the following paragraph:

4. 1. Z-Scan Measurements

The Z-scan experiments were performed using a continuous wave (CW) diode solid state laser at 473 nm wavelength and 20 mW power, which was focused by (15 mm) focal length lens. The schematic of the experimental set up used is shown in Figure (5). A(1 mm) wide optical cell containing the solution of (Di-Cinnamylidene Benzidine) is translated across the focal region along the axial direction that is the direction of the propagation laser beam. The transmission of the beam through an aperture placed in the far field was measured using a photodetector fed to the digital power meter. There are two methods of Z-Scan technique, closed aperture to obtain nonlinear refractive coefficient ,and open aperture method to obtain nonlinear absorption coefficient. The far field intensity is measured as a function of the sample position by properly monitoring the transmittance change through a small aperture at the far field position (closed aperture), by moving the sample through the focus and without placing an aperture at the detector(open aperture) [12].

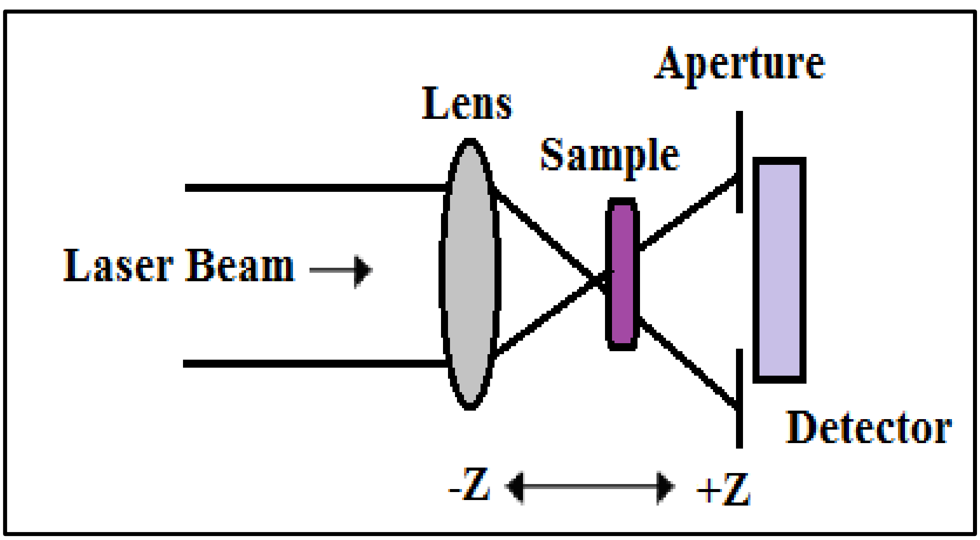

Fig. 5. Schematic diagram of experimental arrangement for the Z-Scan measurement.

The third-order nonlinear refractive index n_2 ,and the nonlinear absorption coefficient, β, of the (Di-Cinnamylidene Benzidine) in ethanol solvent at different concentrations were evaluated by the measurements of Z-Scan. The intensity at the focal spot is (I_o = 20.408 kW/cm^2).

4. 2. Nonlinear Optical Properties

The nonlinear properties w ere measured by extracting the nonlinear refractive coefficient (n_2) by closed-aperture Z-Scan measurements and nonlinear absorption coefficient (β) by open-aperture Z-Scan. The nonlinear refractive index of the (Di-Cinnamylidene Benzidine) in ethanol solvent at different concentrations (9×10^{-5}, 8×10^{-5}, 7×10^{-5}, 6×10^{-5}, 5×10^{-5} and 4×10^{-5}) M, were measured by the Z-Scan technique. The measurements were done at 473 nm, 20 mW. Figure (7) shows closed-aperture Z-Scan at different concentrations of (Di-Cinnamylidene Benzidine) in ethanol solvent at 473 nm, 20 mW, the nonlinear effect region is extended from (-5) mm to (5) mm and the transmittance difference between peak and valley, ΔT_{p-v} at concentrations (9×10^{-5}, 8×10^{-5}, 7×10^{-5}, 6×10^{-5}, 5×10^{-5} and 4×10^{-5}) M equals to (0.038, 0.032, 0.027, 0.021,0.015 and 0.011) respectively. High transmittance is (0.9657) and low transmittance is (0.8823) at concentration (9×10^{-5}) M. The peak followed by a valley transmittance curve obtained from the closed aperture Z-scan data indicates that the sign of the refraction nonlinearity is negative ($n_2 < 0$), leading to self-defocusing lensing in the sample.

In order to describe the Z-Scan behavior in the previous figures, when the sample moves far from the focus, the transmitted beam intensity is low and the transmittance remains relatively constant. As the sample approaches the beam focus, intensity increases, leading to self-lensing in the sample tend to collimate the beam on the aperture in the far field, increasing the measured transmittance at the iris position. If the beam experiences any nonlinear phase shift due to the sample as it is translated through the focal region, then the fraction of light falling on the detector will vary due to the self-lensing generated in the material by the intense laser beam. In this case, the signal measured by detector will exhibit a peak and valley as the sample is translated .

The position of the peak and valley, relative to the z-axis, depends on the sign of the nonlinear phase shift .Where the change in the normalized transmittance from the peak of the curve to the valley ΔT_{p-v} is directly proportional to the nonlinear phase shift imparted on the beam. Moreover, if the beam is transmitted through the nonlinear medium the induced phase shift can also be either negative or positive accordingly when the medium is self- defocusing or self-focusing, respectively. The magnitude of the phase shift can be determined from the change in transmittance between peak and valley. After the focal plane, the self-defocusing increases the beam divergence, leading to a widening of the beam at the focus and thus reducing the measured transmittance. Far from focus ($z > 0$), again the nonlinear refraction is low resulting in a transmittance z-independent. The behavior of Z-Scan curves was in good agreement with [9,11].

To investigate the nonlinear absorption coefficient, Figure (7) shows open-aperture Z-Scan for (Di-Cinnamylidene Benzidine) in ethanol solvent at different concentrations at 473nm, 20 mW.

Its noticed the valley was smaller and the minimum transmittance T(z) are (0.8620, 0.8470,0.8230,0.8000,0.7800 and 0.7400) at different concentrations (9×10^{-5}, 8×10^{-5},7×10^{-5}, 6×10^{-5}, 5×10^{-5}, and 4×10^{-5}) M respectively, also from Figure (7) noticed two photon absorption phenomenon. This behaviour is in agreement with [9,11].

In order to represent the behavior of the material when it is put in the open z-scan system, must follow the following steps. At different distances from the far field of the sample position (-Z), the transmittance is constant with distance. At the near field the transmittance curve begins to decrease until it reaches the minimum value T(z) at the focal point, where (Z = 0) mm. The transmittance begins to increase toward the linear behavior at the far field of the sample position (+Z). The change of the intensity in this case is caused by two photon absorption in the sample travels through beam waist.

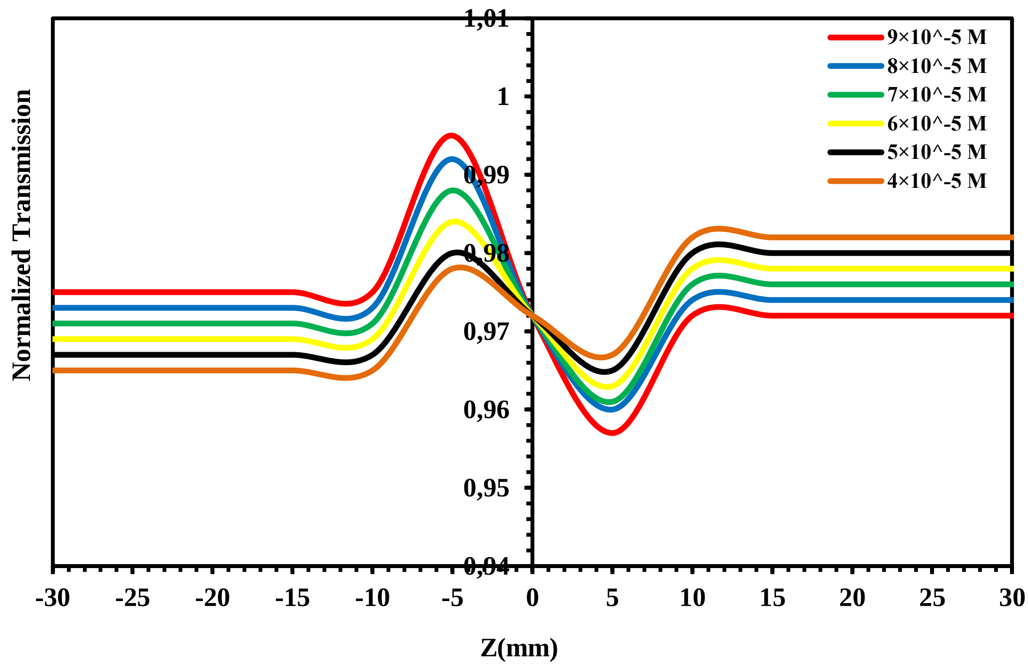

Fig. 6. Closed-aperture Z-Scan data for (Di-Cinnamylidene Benzidine) in ethanol solvent at different concentration.

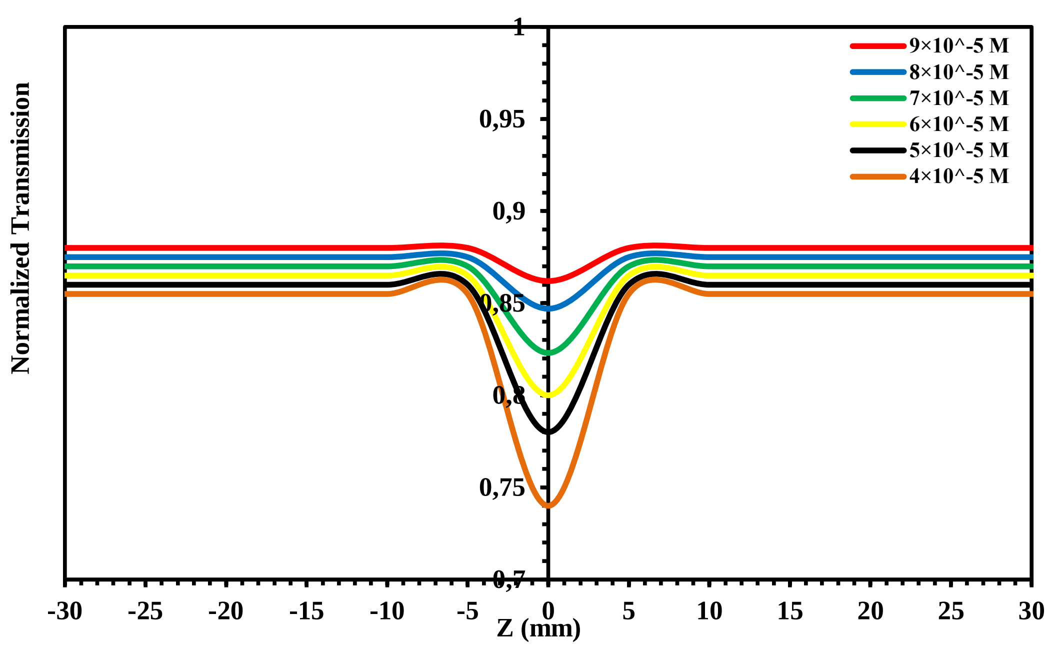

Fig. 7. Open-aperture Z-Scan data for (Di-Cinnamylidene Benzidine) in ethanol solvent at different concentration.

The nonlinear parameters are calculated, as tabulated in Table (1), from this Table we show that the values of nonlinear parameters (n_2 and β) are decreased with decreasing the concentrations of (Di-Cinnamylidene Benzidine) in ethanol solvent, as decreasing the values of linear parameters (α_o and n_o). This is due to decreasing number of molecules per volume unit at low concentrations.

Table 1. The nonlinear optical parameters for (Di-Cinnamylidene Benzidine) in ethanol solvent at different concentrations.

Concentration $\times 10^{-5}$ (M)	**Linear Transmission T**	**Linear Absorption Coefficient α_o (cm^{-1})**	**Linear Refractive Index $n_\circ$**	**ΔT_{p-v}**	**$\Delta\varphi_\circ$**	**n_2 $\times 10^{-10}$ (cm^2/mW)**	**T(z)**	**β $\times 10^{-3}$ (cm/mW)**
9	0.8823	0.1252	1.6668	0.038	0.0935	3.4750	0.8620	1.1946
8	0.8975	0.1081	1.6054	0.032	0.0788	2.7434	0.8470	1.1750
7	0.9270	0.0757	1.4829	0.027	0.0666	2.4666	0.8230	1.1372
6	0.9501	0.0511	1.3808	0.021	0.0517	1.8937	0.8000	1.0912
5	0.9545	0.0464	1.3597	0.015	0.0369	1.3566	0.7800	1.0682
4	0.9657	0.0348	1.3039	0.011	0.0270	1.0030	0.7400	1.0204

4. 3. Optical Limiting Behavior

Optical limiting occurs when the optical transmission of a material saturates with increasing laser intensity, a property that is desirable for the protection of sensors and human eyes from the intense laser radiation. The optical power limiting property of the (Di-Cinnamylidene Benzidine) in ethanol solvent at different concentrations, is measured with the same laser used in Z-Scan technique. Additionally a varying beam splitter was used to vary the input power. Figure (8) gives the optical limiting characteristics at room temperature for the sample. The sample shows very good optical limiting behavior arising from nonlinear refraction. The output power rises initially with the increase in input power, but after a certain threshold value, the sample starts defocusing the beam resulting in a greater part of the beam cross-section being cut off by the aperture. Thus the transmittance recorded by the photodetector remained reasonably constant showing a plateau region. From the threshold intensity for optical limiting for each sample, the optical power limiting threshold is inversely proportional to the concentration. This indicates that the properties of optical limiting become better with increasing the concentrations. This behavior is in agreement with [9].

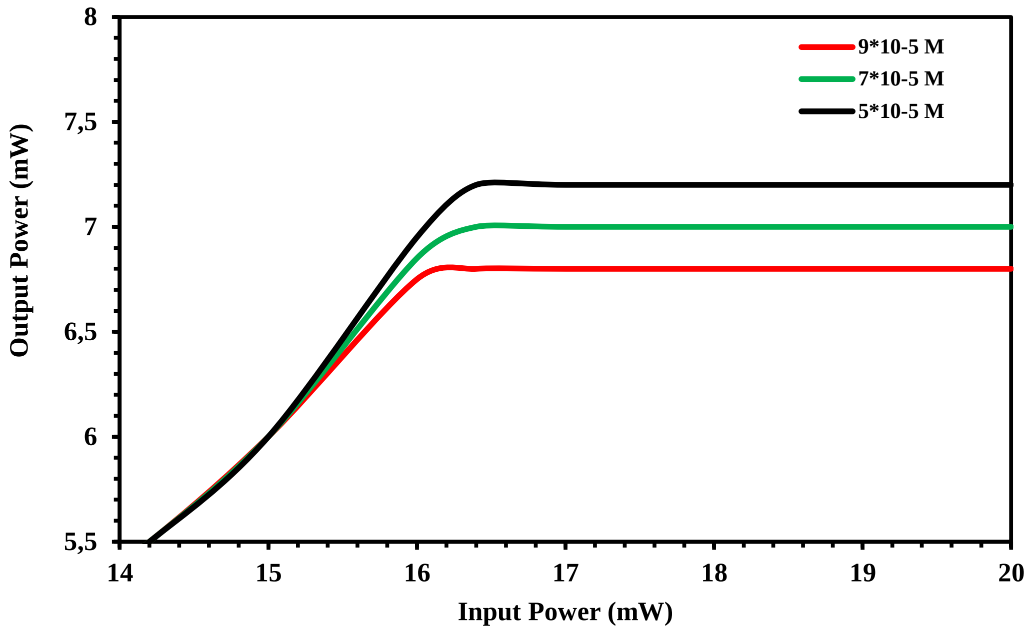

Fig. 8. Optical limiting response (Di-Cinnamylidene Benzidine) in ethanol solvent at different concentrations at 473 nm.

4. CONCLUSIONS

We have measured the nonlinear refraction index n_2 and the nonlinear absorption coefficient β for the solutions of (Di-Cinnamylidene Benzidine) in ethanol solvent for different concentrations, using the Z-Scan technique with 473 nm of (CW) laser. The Z-Scan measurements indicated that the material exhibited large nonlinear optical properties. We have shown that the nonlinear absorption can be attributed to a two photon absorption process, while the nonlinear refraction leads to self-defocusing in this material. All the solutions samples showed a large nonlinear refractive coefficient and nonlinear absorption coefficient of the order of 10^{-10} cm^2/mW and 10^{-3} cm/mW, respectively, the optical limiting behavior has been studied. All these experimental results show that the solution (Di-Cinnamylidene Benzidine) is a promising material for applications in nonlinear optical devices.

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