# Nonlinear Optical Properties and Optical Limiting Measurements of Ethyl 2-[(E)-4-(dimethylamino)benzylidenehydrazino]-5-Nitrobenzoate under cw Laser Regime

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**Abstract:** We report results from investigation of the nonlinear refractive index and nonlinear absorption coefficient of Ethyl 2-[(E)-4-(dimethylamino) benzylidenehydrazino]-5-nitrobenzoate ((DMBH5NB)) solution using z scan technique with a continuous wave (cw) Argon ion laser. The results show that this type of organic material has a large nonlinear absorption and nonlinear refractive index at 488nmd and 514nm. The origin of the nonlinear effects was discussed. We demonstrate that the light induced nonlinear refractive index variation, leads to limiting effect. The results indicated that DMBH5NB could be promising candidates for application on nonlinear photonic devices and optical limiters.

**Keywords:** Nonlinear optics, Optical limiting, Nonlinear refractive index**.**

## 1- Introduction

In general the variation of optical properties of materials induced by high intensity light is divided into light induced absorption changes and light induced refractive index changes: The light induced absorption changes are commonly describe by $\alpha = \alpha_o + \beta I$, where $\alpha$ is linear absorption coefficient, I is the intensity of the light and $\beta$ is a nonlinear absorption coefficient. This coefficient contains interesting nonlinear optical effects such as: Reverse Saturation Absorption (RSA), Two Photon Absorption (TPA), and Saturation Absorption (SA). The light induced refractive index changes are described by the relationship $n = n_o + n_2 I$, where $n_o$ is the linear refractive index, I is the intensity of the light and $n_2$ is a nonlinear refractive index coefficient. This coefficient is an effective parameter that contains many interesting nonlinear optical effects, such as laser induced grating, soliton pulse propagation in waveguides [1, 2], optical switching [3-5] a self-focusing, self-defocusing, self-phase modulation, self diffraction, optical bistability and optical limiting [6-9].

A large number of materials have been found to exhibit laser induced refractive index changes such as fullerenes, liquid crystals, natural substances such as Henna, Chinese tea and Curcumin and organic materials such as Porphyrin, Phthalocyanine and their derivatives. Among Organic materials, Hydrazones and their derivatives have recently attracted much attention due to their high tendency to crystallize in asymmetric structure and for their synthetic flexibility that can offer the modification of nonlinear properties. The nonlinear optical response of this type of materials can be enhanced by following suitable synthetic procedures to design molecules with delocalize $\pi$ electrons, donor - accepter – donor (D-A-D) and acceptor- donor- acceptor (A-D-A) properties[10-12]. The nonlinear properties and optical limiting behaviours of these type of materials were investigated using nanosecond and femtosecond laser pulses [10]

In this work, we report the experimental measurements of nonlinear refractive index and the nonlinear absorption of DMBH5NB solution with continuous wave (cw) argon ion laser at 488 nm and 514 nm

(power 10mW ) using the Z- scan technique [13]. The optical limiting behaviour based on nonlinear refractive index was also investigated.

## 2-  Synthesis

Ethyl 2-[(E)-4-(dimethylamino)benzylidenehydrazino]-5-nitrobenzoate (DMBH5NB) was obtained by refluxing ethyl 2-hydrazinyl-5-nitrobenzoate (0.01mol) and 4-(dimethylamino) benzaldehyde (0.01mol) in ethanol (40ml) by adding 3 drops of concentrated sulfuric acid for 8 hrs. Excess ethanol was removed from the reaction mixture under reduced pressure. The resulting crude after synthesis reaction was collected by filtration, dried and purified by repeated crystallization from acetone[14]. The structure of the compound is shown in Fig.1.
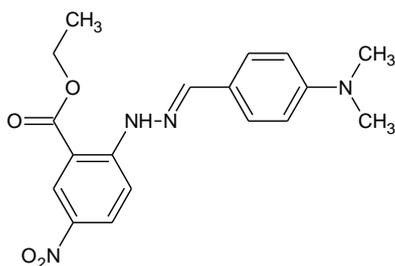


**Fig.1 Chemical structure of DMBH5NB compound**

## 3-  Experimental Procedure:

Solutions of different concentrations for the sample were prepared in dimethylformamide (DMF) and placed in 1mm cuvette. The linear absorption spectra of the sample were recorded with a Shimadzu UV-1800 spectrometer. The linear absorption spectrum for the sample at the concentration 0.25 g/l is shown in Fig.2. The spectrum shows absorption peaks at 331 nm and 434 nm.
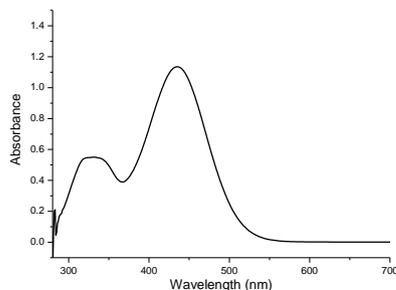


**Fig. 2.  Linear absorption spectrum of DMBH5NB compound in DMF.**

The Z-scan technique [13] was used to measure the nonlinear refractive index. This technique relies on the fact that the intensity varies along the axis of the convex lens and is maximum at the focus. Hence, by shifting the sample through the focus, the nonlinear refraction can be measured by observing the spot size variation at the plane of finite aperture /detector combination. The experiment was performed with an air-cooled Ar ion laser beam at 488 nm and 514nm with an average power of 10 mW. The beam was focused to a beam waist of 20 μm with a lens of 5 cm focal length, giving a typical power density range of $1.6 \times 10^7$ W/m$^2$. The transmission for the samples was measured with and without aperture in the far-field of the lens, as the sample moved through the focal point.

## 4-  Results and discussion

Figure 3 shows a typical normalized transmission at wavelengths 514nm (closed Z-scan) for sample, as a function of the sample position: The normalized transmittance curves for all samples were characterized by a prefocal peak followed by a postfocal valley. This peak valley configuration implies that the nonlinear refractive index of solution is negative ($n_2 < 0$) (self defocusing). Similar characteristics were shown by the sample studied at 488nm. The observed asymmetric nature of the z-scan measurements a long with fact that the laser beam used in the experiment is a CW, peak valley configuration suggests that the nonlinear refractive index observed is of thermal-origin [15]. The nonlinear refractive index effect may arise from different physical mechanisms such as electronic (Kerr effect) or thermal effect (focusing and defocusing). The nonlinear refractive index for all samples in this case may be attributed to a thermal nonlinearity resulting from the absorption of incident beam by the medium which results in deposition of heat via non-radiative decay from excited states where a transverse temperature gradient is established due to the temperature coefficient of the refractive index (dn/dt). The produced refractive index gradient creates a lens like optical element, a thermal lens (thin lens in Z scan), resulting in the phase distortion of the propagating beam at the farfield. Moreover the fit of the Z-scan data to Eq. (1) gives the value of the Rayleigh range $Z_0 = 4.3$ mm. The peak–valley distance of the Z-scan curve for Kerr-like media is $Z_{p-v} = 1.7 Z_o$ ; however, for our case, $Z_{p-v} = 2.2 Z_0$. This is another indication that the nonlinearity in this case is of thermo-optic origin.

The normalized transmission of closed aperture Z scan is given by [15]

$$T = (1 + \emptyset \frac{2x}{1+x^2} + \emptyset^2 \frac{x}{1+x^2})^{-1} \qquad (1)$$

Where x= z/z$_o$(with $z_o = \pi w_o^2 / \lambda$ ) is the diffraction length of the Gaussian beam, $w_o$ is the beam waist at focus and $\phi$ is the nonlinear phase change.. The normalized closed aperture Z scan data are fitted with Eq. 3 to obtain φ values. The nonlinear refractive index n$_2$ is then related to φ by [13]

$$n_2 = \frac{\emptyset \alpha \lambda}{2\pi I_o (1 - e^{-\alpha l})} \qquad (2)$$

where α is the linear absorption coefficient at 514 nm (α= 0.297/mm) and $l$ is the thickness of the sample. I$_o$ is the peak intensity at the focus, and λ is the wavelength of the laser beam.
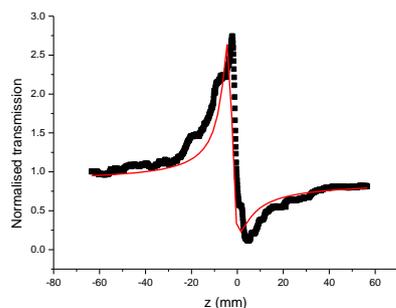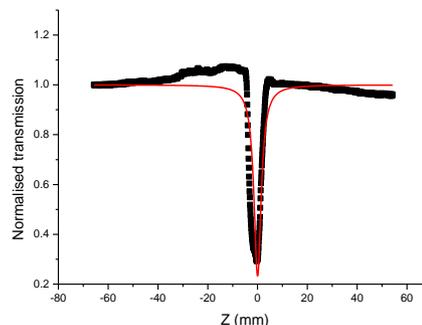


**Fig. 3 Closed-aperture Z-scan for DMBH5NB compound in DMF at 514 nm for 10 mW incident power.**

A fit of equation (1) to the experimental data is depicted in fig.(3), and yields the value of nonlinear refractive index n$_2$ =1.01 x $10^{-11}$m$^2$/W at 514nm. A similar fit was performed to the experimental data at 488nm and yield the values of nonlinear refractive index  n$_2$ =1.49 x $10^{-11}$m$^2$/W. The values reported in this work are in the same order with the values reported for Safranin O Dye and Henna [16, 17], two orders higher than the value reported for Violet 16 dye and CIAI-Phthalocyanine [18-19] and two orders lower than the reported value for Henna [18]. Hydrazones similar to Phthalocyanine, chalcones and C60 are found to be a promising material for various optical devices. Since hydrazones contain the asymmetric transmitter back bone, the compound can be utilized for designing compounds with large third order nonlinear optical properties [10].

Fig.4 shows the normalizing transmission for the open aperture case. The transmission is symmetric with respect to the focus (z =0), where it has minimum transmission. This is an indicative that the sample exhibits reverse saturation absorption, RSA. Similar characteristics were shown by the sample studied at 514nm The conditions required for RSA are as follows: 1- Incident photons with the same wavelength can be absorbed by molecules in the ground state and also by excited states. 2- The absorption of the excited states must be larger than that of the ground state. For most organic molecules excited by a laser wavelength of weak ground state absorption, these conditions are often being met.  In fact the ground state absorption cross section σ$_g$ and excited state absorption cross section were calculated and found that σ$_{ex}$ ℘σ$_g$ . (see below)
Open aperture Z-scan was performed also with a pure solvent. In this case, no nonlinear absorption was observed within the limit of the intensity used in the experiment. We conclude that the effect seen is due solute rather than solvent.



**Fig. 4 Open-aperture Z-scan for DMBH5NB compound in DMF at 488 nm for 10 mW incident power**

The normalize transmittance for the open aperture is given by [13].

$$T(z) = 1 - \frac{\Delta \varphi}{(1 + x^2)} \qquad (3)$$

Where x= z/z$_o$(with $z_o = \pi w_o^2 / \lambda$ ) is the diffraction length of the Gaussian beam, $w_o$ is the beam waist and $\Delta \varphi$ is the nonlinear phase change. The nonlinear absorption β is then related to $\Delta \varphi$ by [13]

$$\beta = \frac{2\sqrt{2}\Delta\varphi\alpha}{I_o(1-e^{-\alpha l})} \qquad (4)$$

where $\alpha$ is the linear absorption coefficient at $\lambda$ =488 nm ($\alpha$= 0.41/mm), l is the thickness of the sample and $I_o$ is the peak intensity at the focus. A fit of equation (4) to the experimental data is depicted in the Fig.(4), and yields the value of nonlinear absorption $\beta$ = 1.95x10$^{-4}$ m/W at 488nm. A similar fit was performed on the experimental data for 514nm which yielded the value of nonlinear absorption $\beta$ = 6.42x10$^{-5}$ m/W. These values are two orders smaller than the values reported for zinc porphyrin polymer measured with Z- scan method [20] and one order lower than the value reported for tris(acetylacetonato) manganese(III) [21] The nonlinear absorption coefficient ® is related to the excited-state absorption given by [22]

$$\beta = \frac{\lambda N_o \Delta\sigma}{4\pi I_S} \qquad (5)$$

where $\otimes \int = \int_{ex} - \int_g$ is the difference between the excited-state absorption cross section $\int_{ex}$ and the ground-state absorption cross section $\int_g$, $N_0$ is the total concentration ($N_0 = 2.14 \times 10^{17}$ cm$^{-3}$), and $I_s = hc/\perp\int_g|$, where $hc/\perp$ is the pump-photon energy, $\perp$ is the excited lifetime and taken to be 1ms triplet state. The ground-state absorption cross section was calculated from $\int_g = \langle_0 /N_0$ and found to be $4.38 \times 10^{-17}$ cm$^2$. Using Eq. (5), the excited-state absorption cross section was calculated and found to be $\int_{ex} = 2.23 \times 10^{-15}$ cm$^2$. This value is nearly two orders of magnitude higher than the ground-state absorption cross section for 488nm, which is in agreement with the conditions for observing RSA and indicates that the nonlinearity here is associated with RSA. A similar calculations were performed at 514 and found the $\int_{ex}$ is four orders higher than the $\int_g$. This is due to much weaker ground state absorption at 514nm(see Fig.2)

One interesting applications of these materials is optical limiting at low intensity for cw lasers. It has been shown that the optical limiting can be used for the protection of eyes and sensors from high intensity laser beams. Optical limiting is a nonlinear optical process in which the transmitted intensity of the material increases at low incident intensities and at the certain threshold intensity value the transmission remains constant. Optical limiting could arise from thermal defocusing, self diffraction and reveres saturation absorption. In this work the optical limiting experiment based on aperture limited geometry was performed by placing the sample at

post focus position and measuring the transmitted power through the aperture for different incident laser powers. Fig.5 shows the optical limiting curve where the transmission is plotted as a function of input power for 0.25g/l solution for the sample at wavelengths 488nm an 514 nm samples. As can be seen from Fig.5, at low power region the output power increases with an increase in input power. At a certain threshold value the defocusing effect occurs, which results in a greater cross section area and reduces the proportional intensity of the beam passing the aperture. Thus the transmittance recorded by the detector reduced considerably. The limiting effect of the samples occurred at a threshold power value of 2.7mw for 488nm and 4.84mW for 514nm and measured from deviation of linearity. The values obtained here depend on experimental setup parameters such as the focusing lens and the distance between the sample and the detector and the absorption at the probe wavelength.
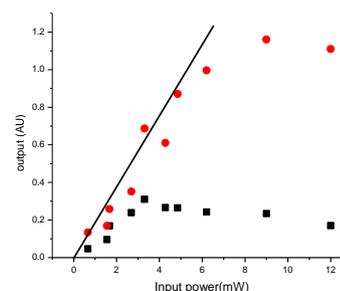


**Fig.5 Optical limiting response of DMBH5NB compound at 514nm (red circles) and at 488 (black squres) .**

### 5-Conclusions:

In conclusion, the nonlinear refractive index and nonlinear absorption coefficient has been measured for ethyl 2-{(2E)-2-[4-(dimethylamino)benzylidene]hydrazinyl}-5-nitrobenzoate in solution using the z scan technique. The origin of the nonlinear refractive index observed in the cw illumination is attributed to the process of thermally induced refractive index change. The nonlinear absorption may be explained by reverse saturation effects. The defocusing effect was used to demonstrate the optical limiting. The values obtained in this work can be improved creating (D-A-D) design and (A-D-A) design in the molecules. Low power pumping is important for device manufacturing with respect to cost, compactness and threshold damage. The ethyl 2-{(2E)-2-[4-(dimethylamino)benzylidene]hydrazinyl}-5-nitrobenzoate investigated in this work seems to be

promising candidates for future photonic and optoelectronic devices

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