Canadian Journal of Physics
Revue canadienne de physique

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Journal:	<i>Canadian Journal of Physics</i>
Manuscript ID	cjp-2017-0840.R1
Manuscript Type:	Article
Date Submitted by the Author:	30-Jan-2018
Complete List of Authors:	Khanzadeh, Mohammad; Rafsanjan University of Vali Asr, Physics Dehghanipour, Masoud; Rafsanjan University of Vali Asr Darehkordi, Ali; Rafsanjan University of Vali Asr, Chemistry Rahmani, Fariba; Rafsanjan University of Vali Asr
Keyword:	Z-scan method, Third-order susceptibility, Reverse saturable absorption, Saturable absorption, Nonlinear refractive
Is the invited manuscript for consideration in a Special Issue? :	N/A

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Wavelength-Dependent nonlinear optical properties of 8-(4-methoxyphenyl)-6-oxo-3-p-tolyl-6H-pyrido[1,2-b][1,2,4]triazine-7,9-dicarbonitrile

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Abstract

In this study, 8-(4-methoxyphenyl)-6-oxo-3-p-tolyl-6H-pyrido[1,2-b][1,2,4]triazine-7,9-dicarbonitrile (**A**) was prepared and then the nonlinear optical properties of this compound, including nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) were measured using Z-scan technique by continuous wave laser diode in the wavelengths of 405 nm and 532 nm. In wavelength of 532 nm, by increasing the incident intensity a switch over from saturable absorption (SA) to reverse saturable absorption (RSA) was observed. The results showed that the nonlinear optical properties of this compound depend on the wavelength. It was also observed that with decrease the incident intensity, the thermal nonlinear refractive coefficient increased accordingly, while decreased its thermo-optic coefficient. In addition, the third-order susceptibility of this compound in wavelength of 532 nm was obtained higher than 405 nm.

Keywords: Z-scan method, Third-order susceptibility, Reverse saturable absorption, Saturable absorption, Nonlinear refractive.

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1. Introduction

Nowadays, the nonlinear optics become one of exciting fields in optics. Materials with eligible nonlinear optical (NLO) properties are used in optical sensors, Q-switched laser and optical limiting applications [1-5]. By studying the NLO properties can be found the more suitable materials for such applications. There are different methods to measuring the NLO properties of materials such as four wave mixing, three wave mixing, and Z-scan [6-8]. Vast studies have been carried out on this phenomenon such as study of third-order nonlinear optical properties of four dmit complex [9], methyl red [10], graphene covalently functionalized by zinc phthalocyanine [11], tetra tolyl porphyrins [12], zinc tetraphenyl porphyrin [13], dinaphthoporphycenes [14]. Over the last decades there has been an increasing interest and research activity on the NLO properties of organic systems [15-20]. A new photonics technology using optical switching and optical computing instead of, or together with, electronics may well evolve significantly during the coming decades. Strong nonlinearities in organic molecules usually arise from highly delocalized π -electron systems. 8-(4-methoxyphenyl)-6-oxo-3-p-tolyl-6H-pyrido[1,2-b][1,2,4]triazine-7,9-dicarbonitrile (A), with their extensive two-dimensional π -electron system, fulfill this requirement and has been selected for investigation as NLO material. In this research, wavelength dependence of NLO properties of compound A is investigated using Z-scan technique, because there are few studies on dependency of the NLO properties of materials on wavelength [21].

2. Experiment:

2.1. Synthesis of 8-(4-methoxyphenyl)-6-oxo-3-p-tolyl-6H-pyrido[1,2-b][1,2,4]triazine-7,9-dicarbonitrile

8-(4-methoxyphenyl)-6-oxo-3-p-tolyl-6H-pyrido[1,2-b][1,2,4]triazine-7,9-dicarbonitrile (**A**) was prepared by reaction of 1,6-diamino-4-(4-methoxyphenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile and 4-methyl phenyl glyoxal in ethanol and in the presence of boric acid as a catalyst (Fig. 1). This compound decomposes at 327-331 °C and the IR spectra show bands at 1677 and 224 cm^{-1} assigned to C=O and CN groups, respectively.

The structure of compound A was fully characterized and confirmed by NMR, IR and elemental analysis.

M.P = 327-331 decomp. Yield = 93%, IR (KBr, cm^{-1}): 1685, 2219. ^1H -NMR (400 MHz, DMSO- d_6) δ = 9.92 (s, 1H, N=CH), 8.55 (d, 2H, J = 7.2 Hz), 7.88 (t, 2H, J = 7.6 Hz), 7.78 (t, 1H, J = 7.6 Hz), 7.58 (d, 2H, J = 8 Hz), 7.49 (d, 2H, J = 8 Hz), 1.93 (s, 3H, Me). ^{13}C -NMR (100 MHz, DMSO- d_6) δ = 21.52 (Me), 89.53 (CN), 96.80 (CN), 114.87, 115.88, 128.84, 129.98, 130.10, 130.44, 131.17, 131.81, 136.01, 141.57, 141.83, 151.65, 156.00, 157.66, 160.55, 172.48 ppm. Elemental analysis: Value calculated for $\text{C}_{22}\text{H}_{13}\text{N}_5\text{O}$: C, 72.72; H, 3.61; N, 19.27 %, Value found: C, 72.65; H, 3.45; N, 19.13 %.

The photophysical properties of compound A were studied by UV/Vis and fluorescence spectroscopies (Figs. 2 and 3). The emission spectra of 2×10^{-3} M solution of the compound A in DMF at 25 °C is shown in Fig. 2 (Excitation wavelengths: 460 nm) and the absorption spectra of 5×10^{-5} M solution of the compound A in DMF at 25 °C is shown in Fig. 3. The maximum absorption of was located at 346 nm and the synthesized molecule have considerable red light emission located around 650 nm.

2.2. NLO measurements

The Z-scan technique was used to determine the NLO properties of compound A. In this technique the laser beam was focused onto the sample through a 10 mm focal length lens. The light sources used in this experiment were continuous wave laser diodes with 405 nm and 532 nm wavelengths. The beam waist size of these laser diodes at focus for wavelengths of 405 nm and 532 nm using a knife edge experiment were measured 7.62 μm and 11.64 μm , respectively. In all experiments, sample with a concentration of $\frac{1\text{mg}}{6\text{ml}}$ was prepared in DMF solvent and was poured in a quartz cell with 1 mm thickness. Here, the sample was moved by a computerized step-motor along the propagation axis of focused laser beam while its transmission was recorded at each position.

Fig. 4 shows the layout of close aperture (CA) and open aperture (OA) Z-scan experimental apparatus which are the same as that used in our previous research [22]. As shown in Fig. 4, in these arrangements, a spatial filter is used in order to enhance the quality of the laser diode beam and also eliminate the noises from the measuring. Additionally, a beam expander is employed to increase the intensity of the laser beam.

The experimental data obtained from CA Z-scan analysis by fitting the thermal lens model [23, 24], as follows:

$$T_N^{\text{TLM}}(z, \theta) = \frac{1}{1 + \theta \frac{2x}{1+x^2} + \theta^2 \frac{1}{1+x^2}} \quad (1)$$

Where T_N^{TLM} is the normalized transmittance for the CA/OA curve, $x = \frac{z}{z_0}$, z_0 is the Rayleigh range, and θ is on-axis phase shift (the phase difference between the center and the outer edge of the beam). The thermal nonlinear refractive (NLR) index (n_2) can be measured, given by:

$$n_2 = \frac{\theta}{KI_0 L_{\text{eff}}} \quad (2)$$

Where $K = \frac{2\pi}{\lambda}$ is the wave vector, λ is the laser wavelength, I_0 is the laser intensity at focus, $L_{\text{eff}} = \frac{1-e^{-\alpha_0 L}}{\alpha_0}$ is the effective length of the sample, α_0 is the linear (low intensity) absorption coefficient and L is the sample length. Also the curves obtained from OA Z-scan analysis by a model related to both saturable absorption (SA) and reverse saturable absorption (RSA). This model yielding the total absorption coefficient as [22, 25]:

$$\alpha(I) = \frac{\alpha_0}{1+I/I_s} + \beta I \quad (3)$$

Where the first and second terms related to negative nonlinear absorption coefficient (NLA) such as SA and positive NLA such as two photon absorption (TPA) and/or RSA, respectively. In Eq. 3, α_0 is linear absorption, β is positive NLA coefficient, I and I_s are laser radiation intensity and saturation intensity, respectively. The normalized transmittance for the OA curve (T_{OA}) using Eq. 3 can be written as:

$$T_{\text{OA}} = \frac{Q(z)}{\sqrt{\pi}q(z)} \int_{-\infty}^{+\infty} \ln [1 + q(z)\exp(-\tau^2)] d\tau \quad (4)$$

$$\text{Where } Q(z) = \exp\left(\frac{\alpha_0 L I}{I + I_s}\right) \text{ and } q(z) = \frac{\beta I_0 L_{\text{eff}}}{\left(1 + \left(\frac{z}{z_0}\right)^2\right)}.$$

By computing the thermal nonlinear refractive index (n_2) and nonlinear absorption coefficient (β), the real ($\text{Re}(\chi^{(3)})$) and imaginary ($\text{Im}(\chi^{(3)})$) parts of the third-order susceptibility can be obtained as follows [26]:

$$\text{Re}(\chi^{(3)})(\text{esu}) = 10^{-4} \epsilon_0 c^2 n_0^2 n_2 / \pi \quad (5)$$

$$\text{Im}(\chi^{(3)})_{\text{(esu)}} = 10^{-2} \epsilon_0 c^2 n_0^2 \lambda \beta / 4\pi^2 \quad (6)$$

Where ϵ_0 is the permittivity of free space, n_0 is the linear refractive index of the medium, and c is the velocity of light in vacuum. At the end, by measuring n_2 and β at the same intensity, the absolute value of the third-order susceptibility ($\chi^{(3)}$) can be calculated given by [26]:

$$|\chi^{(3)}| = [\left(\text{Re}(\chi^{(3)})\right)^2 + \left(\text{Im}(\chi^{(3)})\right)^2]^{1/2} \quad (7)$$

The linear absorption coefficient (α_0) of the sample was obtained by using Beer's law as follows:

$$I = I_0 \times e^{-\alpha_0 l} \Rightarrow \alpha_0 = -\frac{1}{L} \ln \left[\frac{I}{I_0} \right] \quad (8)$$

Where I_0 and I are the input and output intensity of the sample, respectively. L is the sample length. Here, to simplify, the sample is kept immobile, and subsequently the beam waist size of laser stays constant during the test. Since the beam waist is equal for input and output power, consequently, $\frac{I}{I_0} = \frac{P}{P_0}$ is inserted in Eq. 8. coefficient α_0 for the sample can be obtained by recording the output power versus input power of the sample and using Eq. 8. It is noteworthy that for computing α_0 , the input intensity must be low so that no nonlinear absorption occurs in the sample.

3. Results and discussion

In Figs. 5 and 6, the OA Z-scan curves of the sample are shown in various laser intensities at wavelengths of 405 nm and 532 nm, respectively. As shown in Fig. 5(a), compound A shows a high positive NLA response in $\lambda = 405$ nm. As seen clearly in Fig. 5(b) and Fig. 6, the depth of

valley increases by increasing the input intensity, as a result of enhancement of the NLA response [27-29]. The results of Z-scan curves in Table 1 confirm this statement as well. With increase the input intensity, in nonlinear absorption process, the nonlinear scattering (NLS) plays a role in addition to two-photon absorption (TPA). At high intensity, the contribution of NLS process is increased [30]. In this research, a noticeable scattering was observed in two wavelengths. The source of this scattering can be related to two phenomenon. Firstly, when light is radiated on the matter, the input field interacts with the particles of matter (atom, molecule etc.) and this results to the electrical charges in the matter to fluctuate which leads to light scattering. The second source of scattering is the thermal effects. When compound A absorbs the input light, it gets warm and this heat transfers through the solvent immediately. Then solvent is evaporated and microbubbles are created around the particles of the initial matter. These microbubbles act as a center of scattering deflect the laser beam. In wavelength of 532 nm at low incident intensity, the transmission of the sample when it is located far from the focus of the lens is constant and as it gets close to the focus the intensity increases and electrons are saturated completely in the excited-state absorption. This phenomenon results to saturated absorption (SA) in the sample. In OA Z-scan curve of the sample in $\lambda = 532$ nm (Fig. 6c) a peak related to SA is observed and when the incident intensity is increased to $13.06 \frac{\text{KW}}{\text{cm}^2}$ (Fig. 6a) this peak turned into a valley which is related to reverse saturable absorption (RSA) behavior [31-34]. The observed SA behavior of the sample in wavelength of 532 nm, can be introduced it as a saturable absorber materials such as WS_2 , GO, MoS_2 in Q-switched laser application [35-37]. It should be noted that no switching behavior in NLA response of sample at 405 nm is observed.

Figs. 7 and 8 illustrate the obtained curves from CA Z-scan experiment of compound A in wavelengths of 405 and 532 nm, respectively. The CA Z-scan curves exhibit a peak-valley

signature, indicating the self-defocusing effect. This effect is related to thermal phenomena resulted from absorption of a tightly focused CW laser beam propagating through an absorbing medium and causes a spatial distribution of temperature in the sample solution. When the incident intensity increases, the peak-valley difference also increases but from the data presented in Table 1, it is evident that the NLR index decrease. The same sort of behavior was also reported by Valigatela [38] and Zhang [39]. It is also interesting to note that the thermal nonlinear refractive index (n_2) decrease about 137% and 299% at $\lambda = 405$ nm and $\lambda = 532$ nm, respectively. Decreasing n_2 values with increasing input intensity due to the fact that the NLR responses are not arising from intrinsic third-order nonlinear optical response [40,41].

Here, the value of thermo-optic coefficient ($\frac{dn}{dT}$) of compound A in wavelengths of 405 and 532 nm using the on-axis phase shift, θ , are obtained and listed in Table 1, by the following formula [42,43]:

$$\frac{dn}{dT} = \frac{\lambda K \theta}{\alpha_0 P L_{\text{eff}}} \quad (9)$$

Where K is the thermal conductivity of DMF solvent and its value is set as $0.184 \frac{W}{mK}$, and P is the irradiated laser beam power. According to the results of Table 1, decreasing the incident intensity is due to increase the thermal nonlinear refraction coefficient, while decrease its thermo-optic coefficient.

In order to compare the NLO properties of sample in $\lambda = 405$ nm and $\lambda = 532$ nm from experimental data of Table 1 is used. According to these results, the NLO values of sample in laser intensities of $6.58 \frac{KW}{cm^2}$ and $13.72 \frac{KW}{cm^2}$ at 405 nm were compared with these values in laser intensities of $5.87 \frac{KW}{cm^2}$ and $13.06 \frac{KW}{cm^2}$ at 532 nm. This comparison shows that the NLR index of

sample in $\lambda = 532$ nm is higher than $\lambda = 405$ nm. Also, as shown in Figs. 5 and 6, due to the depth of valley of OA Z-scan curves in different input intensities at $\lambda = 405$ nm is higher than $\lambda = 532$ nm, so the NLA response of compound A in 405 nm is stronger. The results obtained from measuring the real and imaginary parts of the third-order susceptibility and also the absolute value of the third-order susceptibility ($\chi^{(3)}$) of compound A in different intensities and wavelengths are listed in Table 2. According to these results and comparison of NLO properties in two wavelengths, the $\chi^{(3)}$ of sample at $\lambda = 532$ nm is higher than $\lambda = 405$ nm which is due to the greater contribution of real part of $\chi^{(3)}$ in absolute value of $\chi^{(3)}$. The NLA coefficient and NLR index of compound A in this research were obtained $(0.81 - 2.75) \times 10^{-3} \frac{\text{cm}}{\text{W}}$ and $-(11.7 - 42.7) \times 10^{-9} \frac{\text{cm}^2}{\text{W}}$, respectively which are higher than the reported NLO coefficients of graphene oxide (GO) and GO-Ag₂S@ZnS [22], graphene suspended in the water [42] and Ag₂S@ZnS core-shells [44]. Also the NLA coefficient of Tris(2',2-bipyridyl)iron(II) tetrafluoroborate [43] and GO and reduced graphene oxide (rGO) derivatives reported in Ref. 45 are comparable to the obtained results.

4. Conclusions

The results achieved from Z-scan experiments showed that the nonlinear optical coefficients of compound A depend on the wavelength. With decrease the wavelength, the nonlinear absorption coefficient of this compound increased, while its nonlinear refractive index decreased. In addition, the results showed that the thermal nonlinear reflective index of compound A in wavelength of 532 nm is higher than 405 nm. It was also observed that by decreasing the incident intensity in two wavelengths, the thermal nonlinear refractive index of compound A increased, while its thermo-optic coefficient decreased. It is interesting to notice that the

dependency of thermal nonlinear refractive index to intensity was clearer in 532 nm. Also, the results showed that the third-order susceptibility of compound A in 532 nm was higher than 405 nm. Also in wavelength of 532 nm a switch over from SA to RSA behavior in NLA response of sample was observed with increase the input intensity, while this switching behavior in 405 nm was not observed.

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Fig. 1: The structure of 8-(4-methoxyphenyl)-6-oxo-3-p-tolyl-6H-pyrido[1,2-b][1,2,4]triazine-7,9-dicarbonitrile.

Fig. 2: Absorption spectra of 8-(4-methoxyphenyl)-6-oxo-3-p-tolyl-6H-pyrido[1,2-b][1,2,4]triazine-7,9-dicarbonitrile.

Fig. 3: Fluorescence emission spectra of 8-(4-methoxyphenyl)-6-oxo-3-p-tolyl-6H-pyrido[1,2-b][1,2,4]triazine-7,9-dicarbonitrile.

Fig. 4: (a) Z-scan with closed apreture layout. (b) Z-scan with open apreture layout.

Fig. 5: Open aperture Z-scan curve of sample in the intensity of (a) $20.08 \frac{\text{KW}}{\text{cm}^2}$, (b) Different intensities, in the wavelength of 405 nm.

Fig. 6: Open aperture Z-scan curve of sample in the intensity of (a) $13.06 \frac{\text{KW}}{\text{cm}^2}$, (b) $5.87 \frac{\text{KW}}{\text{cm}^2}$, (c) $2.82 \frac{\text{KW}}{\text{cm}^2}$, in the wavelength of 532 nm.

Fig. 7: Closed aperture Z-scan curves of sample in the intensity of (a) $20.08 \frac{\text{kW}}{\text{cm}^2}$ (b) $13.72 \frac{\text{kW}}{\text{cm}^2}$ (c) and $6.58 \frac{\text{kW}}{\text{cm}^2}$, in 405 nm.

Fig. 8: Closed aperture Z-scan curves of sample in the intensity of (a) $13.06 \frac{\text{KW}}{\text{cm}^2}$ (b) $5.87 \frac{\text{KW}}{\text{cm}^2}$ (c) and $2.82 \frac{\text{KW}}{\text{cm}^2}$, in 532 nm.

Table 1

Results of Z-scan curves fitting and thermo-optic coefficient of 8-(4-methoxyphenyl)-6-oxo-3-p-tolyl-6H-pyrido[1,2-b][1,2,4]triazine-7,9-dicarbonitrile.

$\lambda(\text{nm})$	$\alpha_0(\text{cm}^{-1})$	$z_0(\text{cm})$	$P_0(\text{mW})$	$I_0(\frac{\text{KW}}{\text{cm}^2})$	$n_2(\frac{\text{cm}^2}{\text{GW}})$	$(\frac{dn}{dT}) \times 10^{-5}(\text{K}^{-1})$	$\beta(\frac{\text{cm}}{\text{KW}})$	$I_s(\frac{\text{KW}}{\text{cm}^2})$
			18.3	20.08	-11.7	0.73	2.75	125.23
405	20.16	0.045	12.5	13.72	-13.9	0.88	_____	_____
			6	6.58	-16.0	1.01	_____	_____
			27.8	13.06	-14.3	1.48	1.05	14.53
532	5.24	0.080	12.5	5.87	-24.4	2.52	0.97	18.43
			6	2.82	-42.7	4.43	0.81	21.23

Table 2

The absolute value of third-order susceptibility of sample.

$\lambda(\text{nm})$	n_0	$I_0(\frac{\text{KW}}{\text{cm}^2})$	$\text{Re}(\chi^{(3)})(\text{esu})$	$\text{Im}(\chi^{(3)})(\text{esu})$	$ \chi^{(3)} (\text{esu})$
405	1.6	20.08	-7.59×10^{-7}	5.73×10^{-7}	9.53×10^{-7}
		13.72	-9.02×10^{-7}	————	————
		6.58	-1.04×10^{-6}	————	————
		13.06	-9.28×10^{-7}	2.89×10^{-7}	9.72×10^{-7}
532		5.87	-1.58×10^{-6}	6.62×10^{-7}	1.61×10^{-6}
		2.82	-2.77×10^{-6}	6.62×10^{-7}	2.78×10^{-6}