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Third-order nonlinear optical properties of organic azo dyes by using strength of nonlinearity parameter and Z-scan technique

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ABSTRACT

In this paper, two chemically synthesized organic azo dyes, 2-(2,5-Dichloro-phenyazo)-5,5-dimethyl-cyclohexane-1,3-dione (azo dye (i)) and 5,5-Dimethyl-2-tolylazo-cyclohexane-1,3-dione (azo dye (ii)), have been studied from optical Kerr nonlinearity point of view. These materials were characterized by Ultraviolet-visible spectroscopy. Experiments were performed using a continous wave diode-pumped laser at 532 nm wavelength in three intensities of the laser beam. Nonlinear absorption (β), refractive index (n_2) and third-order susceptibility ($\chi^{(3)}$) of dyes, were calculated. Nonlinear absorption coefficient of dyes have been calculated from two methods; 1) using theoretical fits and experimental data in the Z-scan technique, 2) using the strength of nonlinearity curves. The values of β obtained from both of the methods were approximately the same. The results demonstrated that azo dye (ii) displays better nonlinearity and has a lower two-photon absorption threshold than azo dye (i). Calculated parameter related to strength of nonlinearity for azo dye (ii) was higher than azo dye (i), It may be due to presence of methyl in azo dye (ii) instead of chlorine in azo dye (i). Furthermore, The measured values of third order susceptibility of azo dyes were from the order of $10^{-9} esu$. These azo dyes can be suitable candidate for optical switching devices.

1. Introduction

The identification of compounds and materials with nonlinear optical characteristic in the last decades has enticed much attention. These materials can be used in low power lasers for applications in modulators, optical sensors, optical switching, optical limiting and etc [1,2]. Physical mechanisms related to nonlinear optical phenomena is because of electronic and non-electronic (molecular orientation, thermal and etc) processes [3]. In order to measure the nonlinear parameters of materials several methods such as Z-scan technique, degenerate four-wave mixing, ellipse rotation, beam-distortion, to name but a few have been proposed. However, except for Z-scan technique, other techniques require complex experimental apparatuses and set-ups [4–6]. Nonlinear coefficients like nonlinear refraction (NLR), nonlinear absorption (NLA) and third-order susceptibility ($\chi^{(3)}$) can be obtained with high accuracy and simplicity from a single experiment by Z-scan technique [7,8]. Recently, researchers are attempting to find materials with nonlinear optical applications in photonics, nanophotonics and optoelectronics including optical limiting, optical switching, optical computing and etc. Some of these materials such as organic molecules [9], organic dyes [10], and conjugated polymers [11] are investigated by ultra short pulsed lasers [12,13] or continous wave diode-pumped lasers [14,15]. High nonlinearity with low loss as well as fast response time of organic polymers such as oligothienylenevinylenes [16] and some new azo-based polymers such as Iminopyridine ligand [17] and electroactive ligand [18] can be explained by donor-accepter groups, π-electron conjugated systems and etc. Azobanzene polymers are used widely to evaluate the effect of an electron donating and an electron withdrawing groups on the nonlinear response groups in the chain of polymers [19]. Unlike most organic compounds, organic dyes with delocalized electron systems that possess color are of the most interest to chemists and physicists because they (1) have ability to absorb light in the visible spectrum (400–700 nm), (2) have at least one chromophore, (3) have a conjugated system, i.e. a structure with alternating double and single bonds, (4) exhibit resonance of electrons which is a stabilizing force in organic compounds and (5) leading to a high ($\chi^{(3)}$). The ability to absorb light is a special characteristic of dye material, which is correlated to the ground and excited states. The required energy for exciting an electron is calculated according to the Bose-Einstein equation $\Delta E = h\nu = hc/\lambda$. The absorption spectra of a dye molecule consists of multiple absorption bands with different intensities, which overlap with each other. These absorptions are a result of electron transfer from different energy levels. Light absorption of dye materials is in the visible region (400–800 nm). Organic color chemistry is currently undergoing exciting developments due to the opportunities

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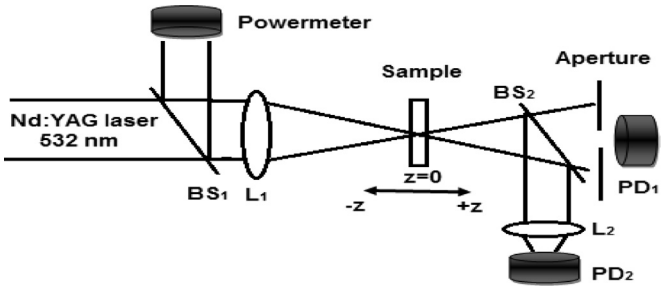


Fig. 1. Schematic diagram of the experimental set-up for the Z-scan technique.

created via dye applications in high-technology fields including electronic devices, linear and nonlinear optics, reprography, sensors and biomedical applications [20]. Studies of tautomeric behavior [21] and nonlinear optical properties [22] of azo dyes are well known.

Azo colorants consist of biological activities arises from their specific metabolisms [23]. They can be found in livers of mammalian creatures [24] in a bacteria of digestive tract [25–27] and in skin bacteria like Staphylococcus aureus [28]. Azo dyes including azo bond –N = N are compounds that obtained from aromatic amino, nitro and nitro particles. Related synthetic methods consist of oxidative/reductive reactions should be one of the major achievements in industrial expansions of organic chemistry that makes them available. Presence of conjugated bonds results color and absorption in the visible light range. Because of the multiform of azo dyes and theirs toxicity in the environment, a new method for biodegradation of them should be find. Most of the azo dyes are important from pharmaceutical, biomedical sights and antiproliferative agents in breast cancer cells. Scientists are trying to treat colon and liver diseases by azo polymers [29]. The base of 2-(2,5-Dichloro-phenyazo)-5,5-dimethyl-cyclohexane-1,3-dione and 5,5-Dimethyl-2-tolylazo-cyclohexane-1,3-dione is dimedone. Dimedone is used for analysis of calorimetry, crystallography, luminescence and spectrophotometric, also it is appropriate case for organic compounds because of their low electrical resistance [30]. This article presents an introduction of azo dyes and their applications, follows by the theory of Z-scan technique and principles of experimental measurements UV–Visible absorption (UV–Vis) in Section 2. The third section includes results and discussion about nonlinear optical absorption and refraction of the azo dyes 2-(2,5-Dichloro-phenyazo)-5,5-dimethyl-cyclohexane-1,3-dione and 5,5-Dimethyl-2-tolylazo-cyclohexane-1,3-dione in three different intensities of the laser beam by two methods and section 4 comprises the conclusions.

2. Experiments and analysis

2.1. NLO measurements

The nonlinear optical properties of azo dyes based on dimedone have been studied by Z-scan technique. The experimental set-up for the Z-scan is depicted in the Fig. 1. The line 532 nm of a continous wave (CW), diode-pumped laser was used in this technique. The TEM_{00} mode of the laser beam was focused by a lens ($f = 10$ cm) and then irradiated on the cell containing the azo dye solution. The cell was moving along the axial direction of the laser beam (z-axis). By recording the data on photodiodes 1 and 2 (PD_1 and PD_2), the nonlinear refractive and absorption indexes of materials can be calculated, respectively. The transmitted beam was monitored as a function of the sample's position (z) in two fast photodiodes. The experiments were performed with three different intensities of the laser beam. The beam radius at the focal plane ($\omega_0 = 62.01$ μm) was obtained by using a charge-coupled device (CCD) camera. The Rayleigh range (z_0) is equal to 22.7 mm, which is calculated by using the relation, $z_0 = k\omega_0^2/2$ and $k = 2\pi/\lambda$ is the wave vector (λ is the laser wavelength). The thickness of the sample cell was less than the Rayleigh range of the beam ($L < z_0$) [31]. Furthermore, the nonlinear coefficients of pure solvent Dimethylformamide (DMF) were measured, as it was several orders of magnitude smaller than the nonlinear coefficients of our samples it was ignored deliberately. For nonlinear studies, two types of organic azo dyes with the chemical names (a) 2-(2,5-Dichloro-phenyazo)-5,5-dimethyl-cyclohexane-1,3-dione (azo dye (i)) and (b) 5,5-Dimethyl-2-tolylazo-cyclohexane-1,3-dione (azo dye (ii)) were chosen and solved in DMF. Azo dyes were prepared so that after mixing aniline and its derivatives (0.03 mol), water (10 ml), concentrated hydrochloric acid (0.09 mol) and aqueous $NaNO_2$ (0.03 mol) the mixture was cooled to 0° > C and was kept at this temperature for 10 min. Then, it was added

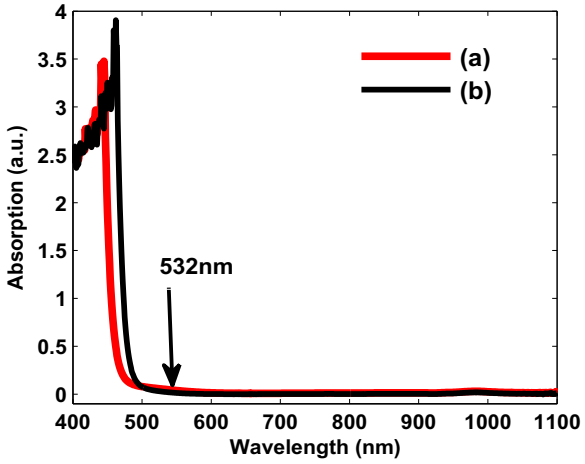
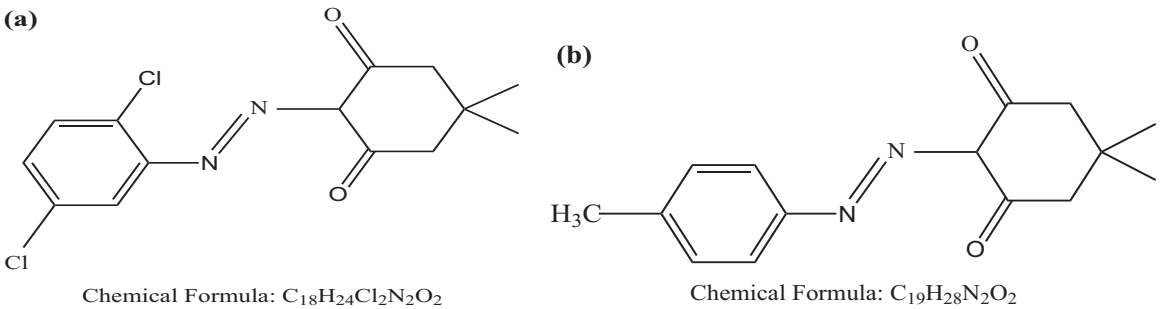


Fig. 3. Absorption spectra of (a) azo dye (i) and (b) azo dye (ii).

Table 1
The measured values of the linear absorption coefficient (α_0) and the linear refractive index (n_0) of the samples.

Samples	$\alpha_0\left(cm^{-1}\right)$	n_0
azo dye (i)	0.114	1.426
azo dye (ii)	0.053	1.427



Chemical Formula: $C_{18}H_{24}Cl_2N_2O_2$ Chemical Formula: $C_{19}H_{28}N_2O_2$

Fig. 2. Molecular structure and chemical formula of the (a) 2-(2,5-Dichloro-phenyazo)-5,5-dimethyl-cyclohexane-1,3-dione and (b) 5,5-Dimethyl-2-tolylazo-cyclohexane-1,3-dione.

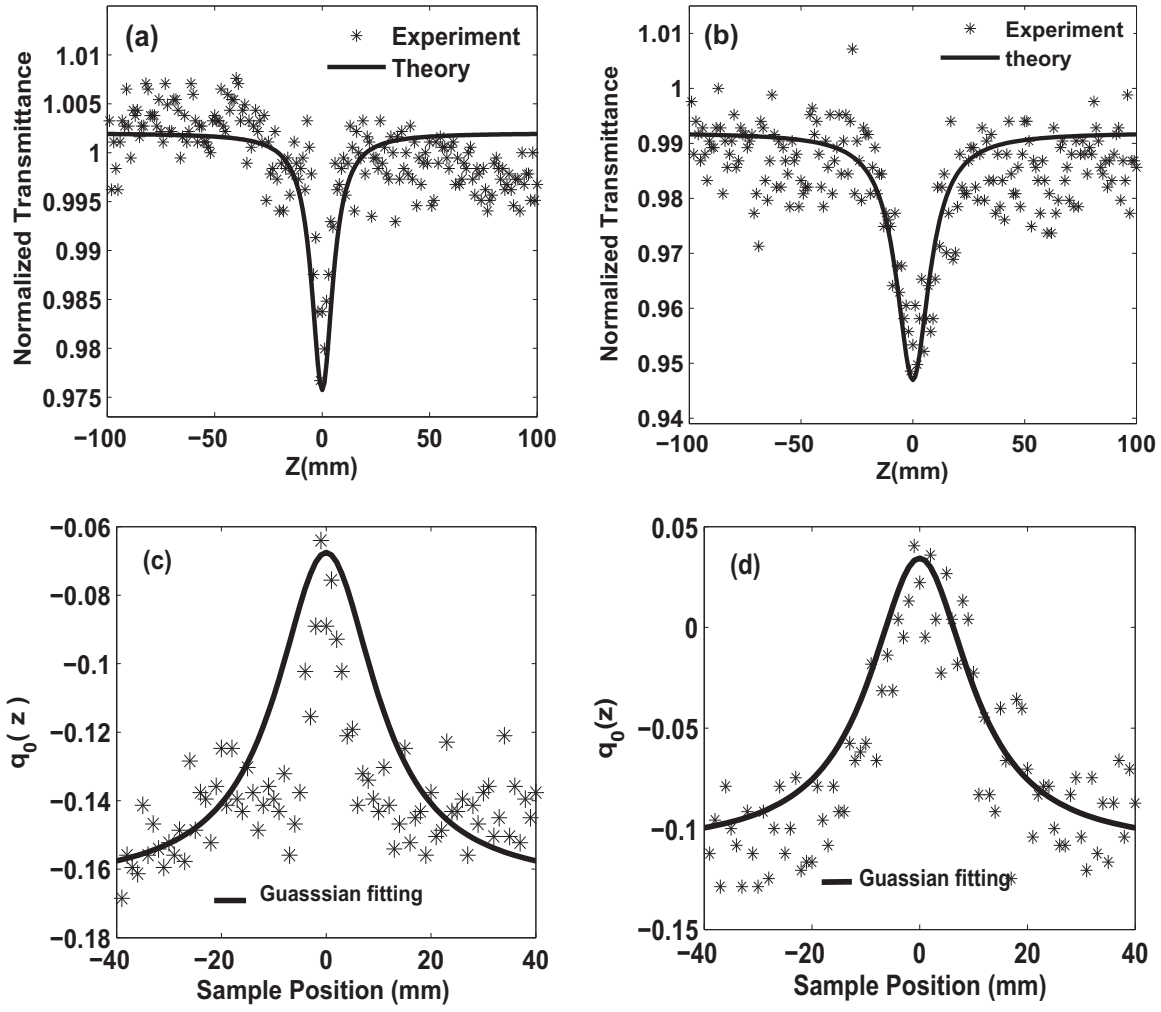


Fig. 4. The open aperture Z-scan curves of (a) azo dye (i) in the 71.98 × 10^3 w/m^2 intensity and (b) azo dye (ii) in the 47.66 × 10^3 w/m^2 intensity. Variation of $q_0(z)$ with sample's position for (c) azo dye (i) and (d) azo dye (ii).

Table 2
Third-order nonlinear optical coefficients of the azo dye (i) in three different intensities.

$I_0(w/m^2)(\times 10^3)$	$n_2(m^2/w)(\times 10^{-11})$	$\beta_{OA}(m/w)(\times 10^{-4})$	$\beta_{q0(z)}(m/w)(\times 10^{-4})$	Re $\chi^{(3)}(esu)(\times 10^{-9})$	Im $\chi^{(3)}(esu)(\times 10^{-9})$	$\lvert\chi^{(3)}\rvert(esu)(\times 10^{-9})$
36.72	−9.92	0	0	5.11	0	5.11
47.66	−22.19	0	0	1.44	0	11.44
71.98	−46.02	1.52	1.134	23.73	21.84	32.25

Table 3
Third-order nonlinear optical coefficients of the azo dye (ii) in three different intensities.

$I_0(w/m^2)(\times 10^3)$	$n_2(m^2/w)(\times 10^{-11})$	$\beta_{OA}(m/w)(\times 10^{-4})$	$\beta_{q0(z)}(m/w)(\times 10^{-4})$	Re $\chi^{(3)}(esu)(\times 10^{-9})$	Im $\chi^{(3)}(esu)(\times 10^{-9})$	$\lvert\chi^{(3)}\rvert(esu)(\times 10^{-9})$
36.72	−7.89	0	0	4.07	0	4.07
47.66	−17.67	4.079	3.784	9.12	16.78	19.09
71.98	−28.02	0	0	14.47	0	14.47

in portions to a solution of benzoylacetone (0.03 mol) in THF (20 ml) and acetic acid. After stirring the mixture for several hours, the precipitated azo dye was filtered off, washed with water and cold isopropyl alcohol and was dried at 20 – 30 °C [32]. The molecular structure and chemical formula of the samples have been shown in Fig. 2 (a) and (b).

2.2. UV–vis spectroscopy

The linear absorption spectra of the organic azo dyes are shown in Fig. 3. Data has been measured in the wavelength region of 400 – 1100 nm. Absorbance values of the samples at the laser's wavelength are 0.050 and 0.023, respectively. The corresponding linear absorption coefficients have been acquired from the following equation.

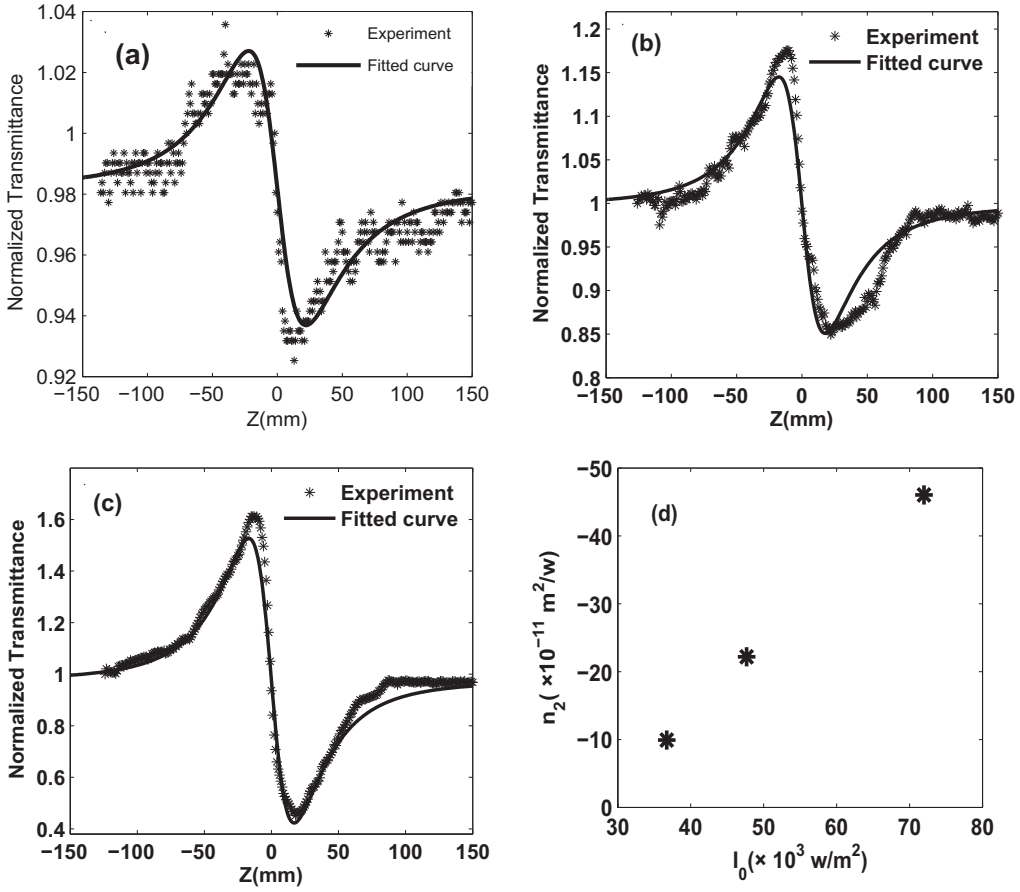


Fig. 5. Closed aperture Z-scan curves of the azo dye (i) under three different laser beam intensities (a) 36.72 × 10^3 w/m^2 (b) 47.66 × 10^3 w/m^2 (c) 71.98 × 10^3 w/m^2 and (d) Variation of n_2 with the laser beam intensity.

$$\alpha = -\frac{1}{L}LnT \tag{1}$$

where, $L = 1$ cm is the cell thickness and T is the transmission of light. Since the linear absorption spectrum is related to the color of organic dye materials and their color is the same, so there isn't significant difference between their spectra. These groups differ in the type of substitute, which do not affect the absorption spectrum. The obtained values of the linear absorption coefficients and linear refractive indexes of samples that were measured by refractometer are listed in Table 1.

3. Results and discussion

By moving the sample through the focus area, the change in the far field intensity with and without an aperture is recorded as a function of the sample's position. In the open aperture for collecting the whole laser beam a lens (L_2) was used. Fig. 4 (a) and (b) illustrates the normalized transmittance for the open aperture Z-scan as a function of z for two azo dyes and Fig. 4 (c) and (d) illustrates the dependence of $q_0(z)$ as a function of sample's position (z). The strength of the nonlinearity parameter $q_0(z)$ can be determined by the normalized transmittance $T(z)$ of the open aperture Z-scan. The values of $q_0(z)$ can be calculated by [33]

$$q_0(z) = \begin{cases} a_0 + a_1T(z) + a_2T^2(z) + a_3T^3(z) & \text{if } T(z) \le 0.75, \\ c_0 + c_1T(z)^{(c_2)} & \text{if } T(z) \ge 0.75, \end{cases} \tag{2}$$

This relation is valid for $T(z) \ge 0.224$ and $T(z) \ge 0.243$ for Gaussian and hyperbolic secant pulses, respectively. Here, the coefficients a_0, a_1, a_2, a_3, c_0, c_1, c_2 for Gaussian pulses have values 15.66, −37.45, 30.76, −8.97, −2.301, 2.156, −1.563, respectively [33]. Calculated parameters related to strength of nonlinearity for azo dye (ii) were higher than azo dye (i). It may be due to presence of methyl in azo dye (ii) instead of chlorine in azo dye (i). There are various mechanisms reported to azo dyes that cause nonlinear absorption, such as multi-photon absorption (MPA), free carrier absorption (FCA), nonlinear scattering and refraction [34,35]. Analyzing the figures near the focus shows that decreased transmissions reveals reverse saturable absorption. It was observed that, in both of the samples, two-photon absorption has occurred in a given intensity and it was completely disappeared as the input intensity increased. The two-photon absorption threshold intensity of azo dye (i) was higher than azo dye (ii). The values of nonlinear absorption coefficient β have been calculated from two techniques and are listed in columns 3 and 4 of Tables 2 and 3. In the first technique, it was obtained from a best fitting, performed on the experimental and theoretical data of the open aperture Z-scan curves in Fig. 4 (a) and (b). These fittings are plotted by the following equation [36].

$$\Delta T(z) \approx 1 - \frac{\beta I_0 L_{eff}}{2\sqrt{2}} \frac{1}{\left(1 + \left(X\right)^2\right)} \tag{3}$$

In this equation, I_0 is the intensity of the laser beam at the focus ($z = 0$), $X = Z/Z_0$ and the sample's effective thickness L_{eff} is given by

$$L_{eff} = \frac{1 - e^{-\alpha L}}{\alpha} \tag{4}$$

where, L is the thickness of the sample and α is the linear absorption coefficient. In the second technique, these values have been determined from the strength of nonlinearity parameter $q_0(z)$ data in Fig. 4(c) and (d) by [37]

$$\beta = \frac{z_R Q_0 \pi}{k P_0 L_{eff}} \tag{5}$$

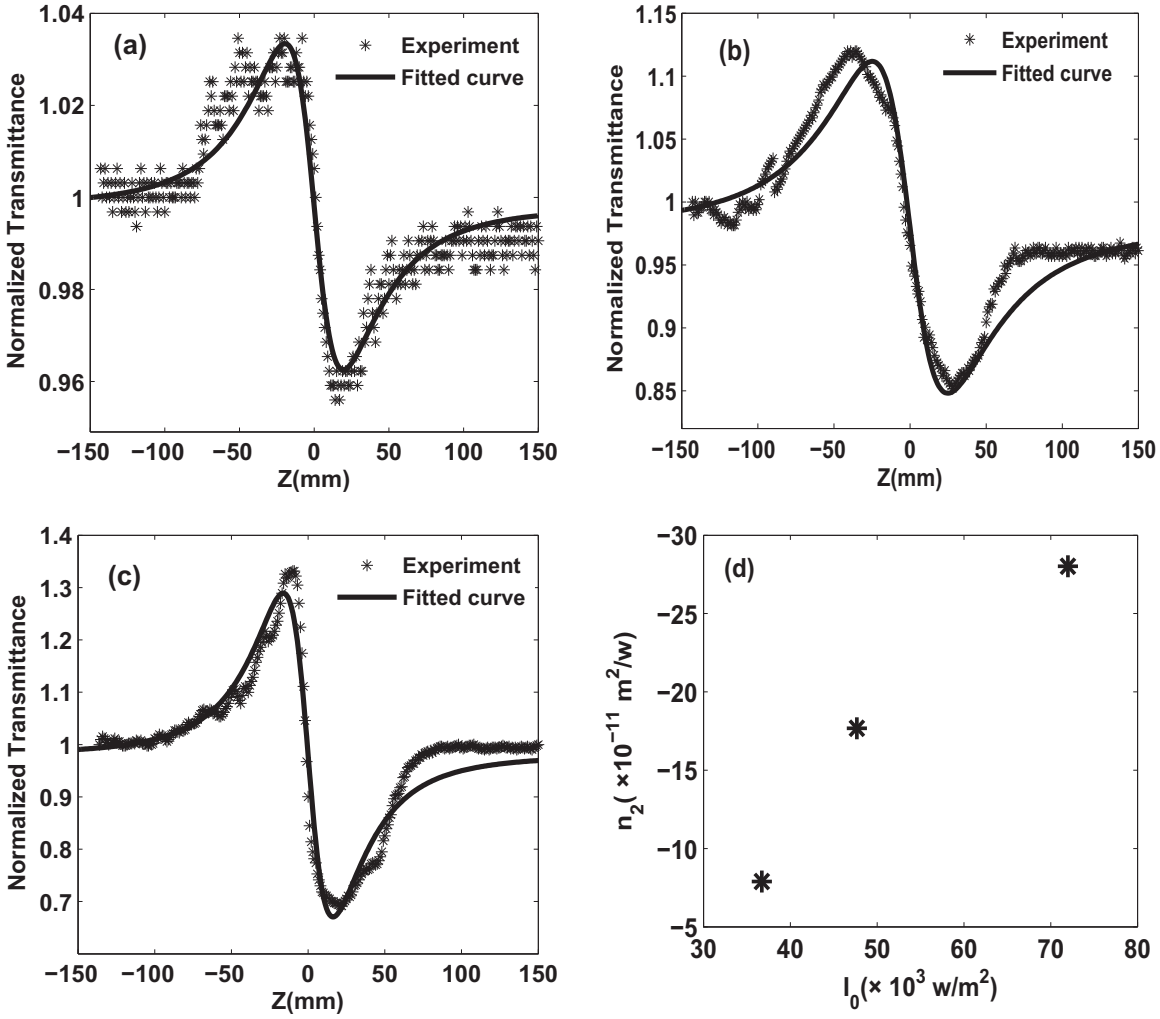


Fig. 6. Closed aperture Z-scan curves of the azo dye (ii) under three different laser beam intensities (a) 36.72 × 10^3 w/m^2 (b) 47.66 × 10^3 w/m^2 (c) 71.98 × 10^3 w/m^2 and (d) Variation of n_2 with the laser beam intensity.

In this equation, Q_0 is the maximum value of $q_0(z)$ in $z = z_0$, P_0 is the peak power of pulses and $2z_R$ is the FWHM of the $q_0(z)$. The values of β obtained from both methods were approximately same together. When the solutions exposed to laser beam, the amount of transmittance from the sample on the detector was changed by Kerr lens generated in the azo dyes. Figs. 5 and 6 show the closed aperture Z-scan data and their theoretical fits. The figures were characterized by a peak followed by a valley (peak-valley) transmittance indicating that the sign of the nonlinear refractive index is negative ($n_2 < 0$) i.e. self defocusing effect has occurred [38]. Since the CW laser normally produces heating effect and defocusing nonlinearity, the nonlinear response is related to variation of refractive index (n) with temperature (i.e., dn/dT). This spatial variation of dn/dT, acts as a thermal lens resulting in the phase distortion of the propagating beam [39,40]. The nonlinear refractive index can be estimated by [41],

$$n_2 = \frac{\Delta T_{P-V}}{0.406\left(1 - S\right)^{0.25} k I_0 L_{eff}} \tag{6}$$

where, $\Delta T_{(P-V)}$ is the difference of peak to valley of transmittance and ($S = 0.2$) corresponds to linear transmittance in aperture that can be determined using,

$$S = 1 - \exp\left(\frac{-2r_a^2}{\omega_a^2}\right) \tag{7}$$

Here, ω_a denotes the beam radius on the aperture and r_a denotes the aperture radius. The theoretical fits of these curves was plotted using [42],

$$T(z) = 1 - \frac{4\Delta\varphi X}{\left(1 + \left(X\right)^2\right)\left(9 + \left(X\right)^2\right)} \tag{8}$$

where, $\Delta\varphi$ is the phase change of the laser beam due to nonlinear refractive that is calculated from $\Delta\varphi = n_2 k I_0 L_{eff}$. The deviation of the fittings of Z-scan curves and the experimental data may have several origins such as absorption in materials that disturbs the symmetry of the closed aperture curves. Although, the Z-scan is a simple technique, but it is sensitive, too. There are some uncertainties in estimating the nonlinear coefficients including errors in measuring focal spot size, linear absorption coefficient, linear refractive index, fluctuations of laser intensity, fluctuations of voltage source, contamination on different points of quartz cell and etc while, the theoretical curves are plotted in perfect conditions without these errors.

The intensity-dependant refractive index of the azo dyes in Figs. 5 (d) and 6 (d) shows that, the difference of peak-valley transmittance increases and the absolute values of nonlinear refractive index enhances as the intensity of laser beam increases. The real and imaginary parts of the third-order nonlinear optical susceptibility $\chi^{(3)}$ and the magnitude of third-order nonlinear susceptibility $|\chi^{(3)}|$ were extracted from the Eqs. (9)–(11) and were listed in Tables 2 and 3 [13].

$$Re\chi^{(3)}(esu) = \frac{10^{-4}\varepsilon_0 c^2 n_0^2}{\pi} n_2(\mathrm{cm^2/W}) \quad (9)$$

$$Im\chi^{(3)}(esu) = \frac{10^{-2}\varepsilon_0 c^2 n_0^2 \lambda}{4\pi^2}\beta(\mathrm{cm/W}) \quad (10)$$

$$|\chi^{(3)}| = \left[\left(Re\left[\chi^{(3)}\right]\right)^2 + \left(Im\left[\chi^{(3)}\right]\right)^2\right]^{1/2}(esu) \quad (11)$$

where, ε_0 is the electric permittivity of free space (8.85×10^{-12} F/m), c is the velocity of light in vacuum and n_0 is the linear refractive index of each sample. The studied azo dyes, consisted of third-order susceptibility as large as $10^{-9}esu$ which could be due to the presence of electron donating and electron withdrawing groups in their chain and the response of delocalized π electrons. Since diode pump continous wave lasers can produce high nonlinearity However, typical values of the nonlinear refractive index of nonresonant electronic, molecular orientation and thermal effects have the order of 10^{-20} m^2/W, 10^{-18} m^2/W and 10^{-10} m^2/W, respectively [3]. It seems that thermal effects have a great portion in collected values of Tables 2 and 3. Since the response time of nonresonant electronic nonlinearites are extremely short, these materials can be used as ultrafast optical switching devices. Being suitable candidate for optical switching is considered by two forms of merit: $W = n_2 I_0/\alpha_0\lambda$ and $T = \beta\lambda/n_2$, that should be $|W| \gg 1$ and $|T| \ll 1$ [43]. These values for azo dye (i) are $|W| = 5.461$ and $|T| = 0.175$ and for azo dye (ii) are $|W| = 7.153$ and $|T| = 0$. The values of W and T in the intensity 71.98 kW/m^2 demonstrate that these organic azo dyes are suitable for all optical switching devices. In comparison with other organic dyes, nonlinear optical susceptibility of these studied dyes ($10^{-9}esu$) is lower than Brilliant Crocein ($10^{-6}esu$) [22] or methyl blue dye ($10^{-6}esu$) [14] and is greater than standard dye IR26 ($10^{-12}esu$) [44].

4. Conclusion

In summary, the third-order nonlinear optical properties of two kinds of azo dyes have been investigated by using a simple and sensitive technique. The samples were dissolved in DMF solvent thoroughly and were evaluated by using open and closed aperture Z-scan techniques and using a continous wave diode-pumped laser at 532 nm wavelength. The experiments were performed with three different intensities of the laser beam. Z-scan measurements express that azo dyes have a negative nonlinear refractive index i.e. self-defocusing effect. Nonlinear absorption coefficients were calculated from two methods; 1) using strength of nonlinearity curves, 2) using theoretical fits and experimental data in the open aperture technique. The values of β obtained from both methods were approximately the same. Samples were characterized using a UV–visible absorption spectra. It was concluded that by altering the inductive electron withdrawing group (chlorine) in 2-(2,5-Dichloro-phenyazo)-5,5-dimethyl-cyclohexane-1,3-dione with inductive electron donating group (methyl) in 5,5-Dimethyl-2-tolylazo-cyclohexane-1,3-dione better nonlinearity and lower two-photon absorption threshold were achieved. As considered by two forms of optical switching merits and due to presence of donor-accepter groups, delocalized π-electrons and etc, causes high nonlinearity in these azo dyes and make them a suitable candidate for optical switching devices. Furthermore, these dyes with good nonlinearity and strong susceptibility may be useful in various technological applications, such as optical switches, novel optical sensors, photonics and electro-optical devices.

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