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Study of the Nonlinear Optical Properties of New Diarylethene Perfluorocyclopentene Derivative by Using Z-scan Technique

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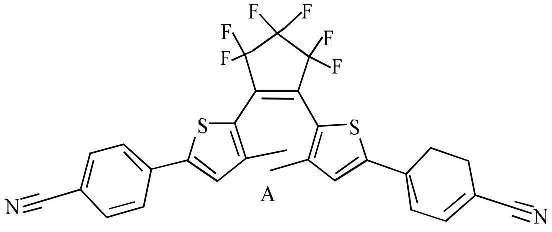
Abstract: The nonlinear optical properties of new organic compound namely 4-(5-{2-[5-(4-Cyanophenyl)-3-methylthiophen-2-yl]-3, 3, 4, 4, 5, 5-hexafluorocyclopent-1-en-1-yl}-4-methylthiophen-2-yl)benzonitrile (A) has been studied by using Z-scan technique with Continuous Wave (CW) diode solid state laser at (473 nm) wavelength and (20 mW) power. Solutions of (A) at (10^{-4} M) were prepared in two different separate solvents (chloroform and acetone) thin film samples of this material were also, prepared via spin-coating technique form (10^{-3} M) solutions from the two solvents separately. The results showed that thin films possess very large nonlinear optical properties as compared with solution samples. For solutions the results imply that acetone solution of this larger nonlinear optical properties as compared with the chloroform solution. The results indicate (A) is a promising material to be used in photonic and nonlinear optical devices.

Key words: Organic materials, Z-scan technique, nonlinear optical properties, methylthiophen, material exhibited, chloroform solution

INTRODUCTION

Materials with nonlinear optical properties have attracted the attention of researchers who are working in the field of nonlinear optics due to the versatile applications of such materials in telecommunications, optical information processing, integrated optics, all-optical limiting, all-optical switching, medical science, laser technology and in other electro optical systems (Suresh *et al*., 2012; Henari and Patil 2014; Shcherbakov *et al*., 2015; Alfalou and Brosseau 2015; Rosenne *et al*., 2015). Beside polymers and inorganic semiconductors, different organic compounds are considered to be important class of materials that have nonlinear optical properties (Boni *et al*., 2010). Many organic compounds that have molecular structures with resonating π-electrons and high dipole moment values have been synthesized to perceive the non linear tendencies more than the inorganic optical materials (Rekha and Ramalingam, 2009). Acid Blue 40 (Pramodini *et al*., 2013) methyl blue (Parvin and Ahamed, 2015) basic fuchsin (Pathrose *et al*., 2016), giemsa (Al-Mudhaffer *et al*., 2016) and benzenesulfonamideazo (Al *et al*., 2016) dyes are examples of the reported organic compounds with interesting optical properties. The photo switchable diarylethene per fluorocyclopentenes are class of organic compounds that have a broad spectrum of applications in molecular switches and other optical devices (Dulic *et al*., 2007). Such, photochromic molecules were reported to have interesting linear and nonlinear optical properties (Pu *et al*., 2006). It is either the radiative, interaction between the optical-electrical field and the active electrons (electronic process) or the non-radiative interactions such as density, temperature and cis-trans isomerism (non-electronic process) that cause of the nonlinear optical phenomena (Sheik-Bahae *et al*., 1990). In the present work we report the use of the Z-scan technique to study the nonlinear optical properties of a new symmetrical diarylethene perfluoro cyclopentene (A) which we have reported its synthesis and characterization in a previously published work (El-Hiti *et al*., 2013). Figure 1 structure of (A).

Theory: The mathematical relationships for nonlinear materials at high intensity of absorption and Nonlinear



A

Fig. 1: The structure of A

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Refraction (NLR) is given by Abdulazeez *et al.* (2016a, b), Abdulaeez and Ban (2016). The absorption of the material at high intensity is given by Eq. 1 (Abdulazeez *et al.*, 2016a, b).

$$\alpha = \alpha_0 + \beta I \tag{1}$$

Where:

I = The incident intensity

α_0 = The linear absorption coefficient

β = The nonlinear absorption coefficient related to the intensity

At high intensity, the refractive index is calculated by Eq. 2 (Abdulazeez *et al.*, 2016a, b).

$$n = n_0 + n_2 I \tag{2}$$

Where:

n_O = The linear refractive index

n_2 = 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 index is 3 calculated from the peak to valley difference of the normalized transmittance according to Eq. 3 and 4 (Abdulazeez *et al.*, 2016a, b).

$$n_2 = \frac{\Delta\Phi_0}{I_0 L_{eff} k} \tag{3}$$

where: $\Delta\Phi_0$ is the nonlinear phase shift

$$\Delta t_{p\text{-}v} = 0.406\left|\Delta\Phi_0\right| \tag{4}$$

Wher:

$\Delta t_{p\text{-}v}$ = The difference between the normalized peak and valley transmittances

$k = 2\pi\lambda/\lambda$ = The beam wavelength

I_0 = The intensity at the focal spot

L_{eff} = The effective length of the sample, determined

$$L_{eff} = \frac{\left(1\text{-}\exp^{-aol}\right)}{\alpha_0} \tag{5}$$

Where:

L = The sample length. The linear absorption coefficient

α_0 = Determined by Eq. 6 (Abdulazeez *et al.*, 2016a, b)

$$\alpha_0 = \frac{\ln\left(\frac{1}{T}\right)}{t} \tag{6}$$

Where:

t = The thickness of sample

T = The transmittance

The linear refractive index (n_0) obtained from Eq. 7

$$n_0 = \frac{1}{T} + \left[\left(\frac{1}{T^2} - 1\right)\right]^{1/2} \tag{7}$$

The intensity at the focal spot is calculated according to Eq. 8.

$$I_0 = \frac{2P_{peak}}{\pi\omega_0^2} \tag{8}$$

It is defined as the peak intensity within the sample at the focus where ω_O the beam radius at the focal point the coefficients of nonlinear absorption (β) can be easily calculated by using Eq. 9 (Abdulazeez *et al.*, 2016a, b).

$$\beta = \frac{2\sqrt{2}T(z)}{I_O L_{eff}} \tag{9}$$

where, T(z) the minimum value of normalized transmittance at the focal point where (z = 0).

MATERIALS AND METHODS

Preparation of solutions: The title compound A was synthesized and fully characterized according to literature procedure (Abdulazeez *et al.*, 2016a, b). Solutions of this material at (10^{-4} M) were prepared by using acetone and chloroform as solvents.

Preparation of thin films: Thin film samples were prepared on a glass substrate by repeat-spin-coating technique from (10^{-3} M) solutions of A in acetone and chloroform solvent.

Linear optical properties: The linear absorption spectra of solutions and thin film samples were recorded at 190-1100 nm wavelengths, using (Aquarius 7000, Optima, Japan) UV-VIS spectrophotometer at room temperature as Fig. 2 and 3, respectively.

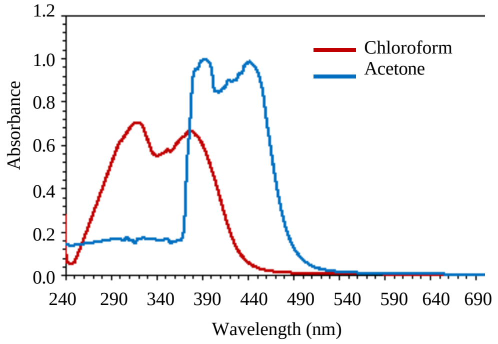

Fig. 2: Absorption spectra for solution of A at (10^{-4} M) in chloroform and acetone solvent

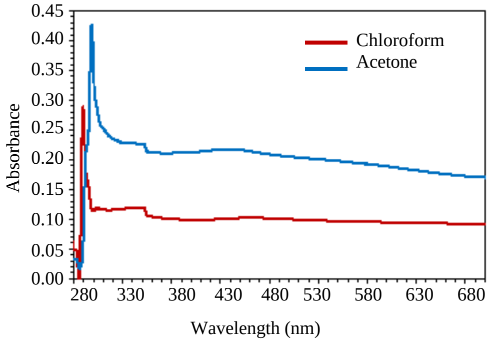

Fig. 3: Absorption spectra for thin films of A at (10^{-4} M) in chloroform and acetone solvent

RESULTS AND DISCUSSION

The Z-scan measurements were measured by a technique which is based on single beam method with inserting a sample in a focused Gaussian beam and translating it along beam axis through a focal region. The far field intensity was 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 aperture at the detector (open aperture). The schematic of the experimental set up used is Fig. 4 and 5.

The nonlinear properties for solutions of A, dissolved in chloroform and acetone solvent at (10^{-4} M) and its thin films at (10^{-3} M) were measured by the Z-scan technique. The nonlinear refractive coefficient (n_2) by closed-aperture Z-scan measurements and nonlinear

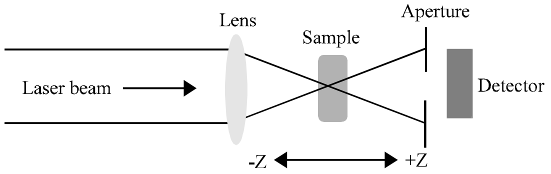

Fig. 4: Schematic diagram of experimental arrangement for the Z-scan measurement

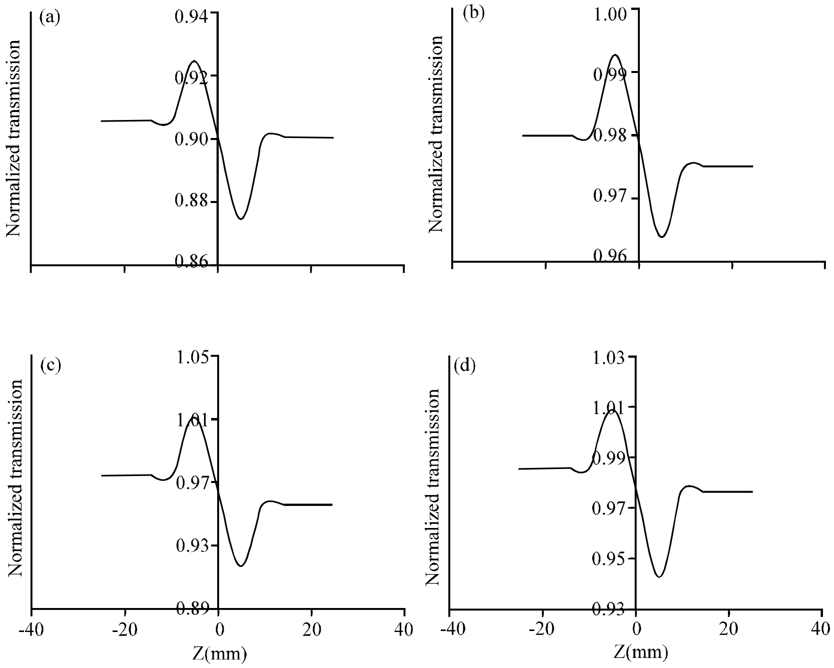

Fig. 5: Closed-aperature Z-scan data for all samples: a) Solution of A in accetone; b) Solutoin of A in chloroform; c) Thin film of A from accetone and d) Thin film of A from chloroform

Table 1: The linear and nonlinear optical parameters for all sampels of A as solutions and thin films

Materials	T	$\alpha_o$cm^{-1}	n_o	ΔT_{p-v}	$\Delta\varphi_o$	n_2 cm$_2$ /mW	T(z)	β cm/mW
Solution of A in acetone	0.4009	0.9138	4.7786	0.050	0.1231	4.7898×10^{-10}	0.860	1.2467×10^{-3}
Solution of A in chloroform	0.9599	0.0408	1.3335	0.029	0.0714	2.6444×10^{-10}	0.800	0.9663×10^{-3}
Thin film of A form acetone	0.6155	48500.2	2.9047	0.100	2.2364	1.0512×10^{-4}	0.908	17.543
Thin film of A form chloroform	0.7908	23459.2	2.0384	0.072	1.4655	502339×10^{-5}	0.595	7.8890

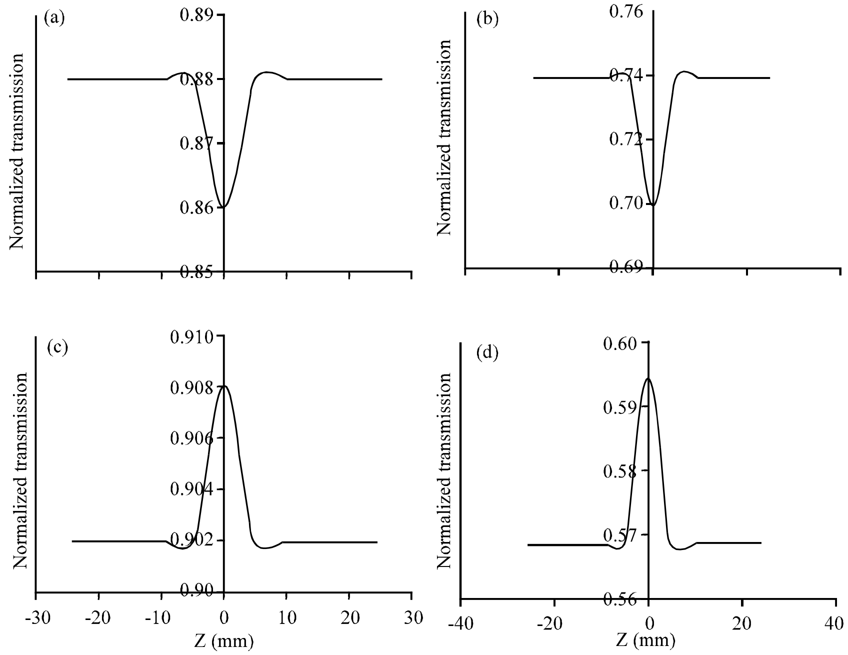

Fig. 6: Open-aperature Z-scan data for all samples of A

absorption coefficient (β) by open-aperture Z-scan. The measurements were done at (473 nm) and (20 mW).

Figures 5a, d shows closed-aperture Z-scan for all samples of this material dissolved in chloroform and acetone solvent. The nonlinear effect region is extended from (-5 to 5 mm). 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.

To investigate the nonlinear absorption coefficient (β), Fig. 6a, d shows open-aperture Z-scan of for all samples of A, dissolved in chloroform and acetone solvent at 473 nm, 20 mW. Its noticed also, from these figures (two photon absorption) phenomenon for samples as solutions and (Saturable absorption) phenomenon were observed for samples as thin films. The nonlinear parameters are calculated as tabulated in Table 1 from this Table 1 we show that the values of linear and nonlinear parameters for samples of A, dissolved in acetone and chloroform solvent as thin films are larger than samples as solutions of the same material.

As well as the linear and nonlinear optical properties for all samples of A, dissolved in acetone solvent are larger than those of the same material dissolved in chloroform solvent.

CONCLUSION

By using Gaussian beam from CW pulsed laser at 473 nm, we studied the nonlinear optical properties of A, dissolved in chloroform and acetone solvent by using Z-scan technique. The nonlinearity of all samples of this material dissolved in acetone solvent is larger than those for the same material dissolved in chloroform solvent. As well as thin films possess very large nonlinearity as compared with samples as solution. The relation between the nonlinear refractive index and the nonlinear phase shift is a linear increasing relation.

Z-scan measurements indicated that all samples of A, dissolved in chloroform and acetone solvent exhibited negative nonlinear refractive index .We also observed that all samples of this material as solutions exhibited (Two photon absorption) behaviour on the other hand all thin films of it exhibited (Saturable absorption) behaviour, the results indicate possibility of using this material in photonic and nonlinear optical devices.

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