



The third-order nonlinear optical properties of novel styryl dyes

Seetharam Shettigar^{a,*}, G. Umesh^b, P. Poornesh^c, K.B. Manjunatha^b, Abdullah Mohammed Asiri^d

^a Department of Physics, NMAM Inst. of Technology, Nitte 574110, Karkala, Karnataka, India

^b Department of Physics, National Institute of Technology, Surathkal 575025, Karnataka, India

^c Department of Physics, Manipal Institute of Technology, Manipal University, Manipal, Udipi 576104, India

^d Department of Chemistry, King Abdul-Aziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

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ABSTRACT

The third-order nonlinear optical properties of two novel styryl dyes, namely, 1,3-diethyl-5-(4-methoxybenzylidene)-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione and 5-(3,4-dimethoxybenzylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione were studied using the Z-scan technique employing 7 ns laser pulses at 532 nm. The nonlinear refractive index, nonlinear absorption coefficient, magnitude of effective third-order susceptibility and coupling factor were determined. The optical power limiting behavior of the colorants was ascribed to two-photon absorption phenomenon. Nonlinear absorption cross-section increased with increase in π electron density and the effective two-photon absorption cross-section was two orders of magnitude larger than those of commercially available azo compounds. The results suggest that these colorants offer promise as nonlinear optical materials for device applications.

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1. Introduction

The nonlinear optical (NLO) properties of organic compounds have been the subject of numerous investigations in recent years due to their potential photonic applications. A good NLO material should generally contain donor and acceptor groups positioned at either ends of a conjugated system of appropriate length; in this context, the extent of this conjugation and, hence, the size of the π delocalised bonds, has been recognized as a factor leading to large third-order nonlinearities. Styryl cyanine dyes and styryl dyes are organic molecules possessing charge donor and acceptor groups, conjugated through π electronic bridge, suitable for NLO device applications [1,2]. They are widely used as optical recording medium in laser disks, laser dyes [3,4] and optical sensitizers in various other fields [5].

This paper presents an experimental investigation of the third-order NLO properties of two organic molecules 1,3-diethyl-5-(4-methoxybenzylidene)-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (SA1) and 5-(3,4-dimethoxybenzylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (SA2), which belong to styryl dyes with methoxy group as the donor and thiobarbituric acid as the

acceptor. Their molecular structure is shown in Fig. 1. To see the effect of acceptor group on nonlinear properties, compound with cyano group as acceptor (SA3) was also taken for investigation.

2. Experiment

2.1. Synthesis and characterization

2.1.1. 1,3-Diethyl-5-(4-methoxybenzylidene)-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (SA1)

Equivalent molar quantities of the benzaldehyde derivative and *N,N*-diethylthiobarbituric acid were dissolved in 25 ml ethanol and heated to reflux. Piperidine (one drop) was added to the solution and reflux was continued for 3 h. The ensuing solution was cooled to room temperature and the solid products were filtered and washed with ethanol (25 ml).

m.pt. 150–152 °C; Yield 95%. Found C, 60.25; H, 5.92; N, 8.68%. Calculated for $C_{16}H_{18}N_2O_3S$, C, 60.36; H, 5.70; N, 8.80%. IR (KBr disk, cm^{-1}) 1693, 1655 (C=O), 1378 (C=S).

¹H NMR ($CDCl_3$, 600 MHz) δ 8.52 (1H, s, Olefinic proton), 8.36 (2H, d, $J = 9.0$ Hz, aromatic protons), 7.00 (2H, d, $J = 9.0$ Hz, aromatic protons), 4.5 (4H, q, 2CH₂N), 3.93 (3H, s, CH₃O), 1.30 (6H, t, 2CH₃CH₂N).

¹³C NMR ($CDCl_3$) 178.9, 164.67, 161.41, 160.15, 158.89, 138.27, 125.85, 117.81, 114, 55.7, 44.17, 43.61, 12.45, 12.40.

* Corresponding author. Fax: +91 8258 281265.

E-mail address: shettigarseetharam@yahoo.com (S. Shettigar).

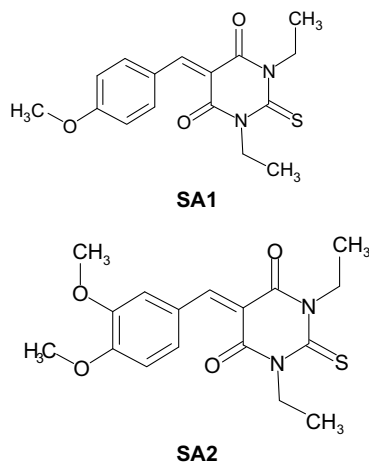


Fig. 1. Structure of styryl dyes.

2.1.2. 5-(3,4-Dimethoxybenzylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (SA2)

m.pt. 185–187 °C; Yield 93%. Found C, 58.42; H, 5.92; N, 7.86%. Calculated for $C_{17}H_{20}N_2O_4S$, C, 58.60; H, 5.79; N, 8.04%. IR (KBr disk, cm^{-1}) 1687, 1655 (C=O), 1372 (C=S).

1H NMR ($CDCl_3$, 600 MHz) δ 8.49 (1H, s, Olefinic proton), 8.34 (1H, d, $J = 1.8$ Hz, aromatic protons), 7.84 (1H, d, $J = 8.4$ Hz, aromatic protons), 6.96 (1H, d, $J = 8.4$ Hz, aromatic protons), 4.5 (4H, q, $2CH_2N$), 3.97, 3.96 (3H, s, CH_3O), 1.30 (6H, t, $2CH_3CH_2N$).

^{13}C NMR, 178.88, 161.49, 160.25, 158.91, 154.68, 148.4, 132.85, 126.17, 116.59, 114.98, 110.44, 56.24, 56.04, 44.21, 43.59, 12.41.

2.2. Nonlinear measurements

30 mg of each molecule was dissolved in research grade DMF to provide a solution of concentration 4.3×10^{-2} mol/L. This sample was placed in a quartz, 1 mm cuvette for the Z-scan measurements [6]. A frequency doubled Q-switched Nd:YAG laser (Model: GCR 170, Spectra-Physics) producing 7 ns pulses of wavelength 532 nm was used as the light source. The input intensity used was 2.39 GW/cm². To obtain open-aperture data, the intensity transmitted by the liquid sample was measured as a function of sample position along the Z-axis. Closed-aperture data was obtained using an aperture ($S = 0.5$) in front of the detector. Optical limiting experiment was also carried out on these moieties to assess them as possible photonic material for optical limiting applications. The linear absorption spectrum of the samples was recorded using fiber optic spectrometer (model SD 2000, Ocean Optics Inc) in the

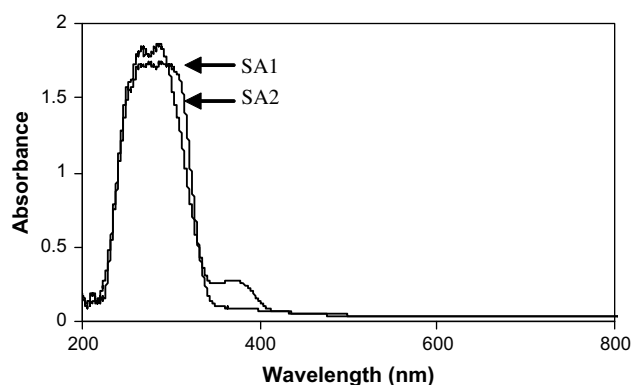


Fig. 2. UV-vis absorption spectra of the styryl dyes.

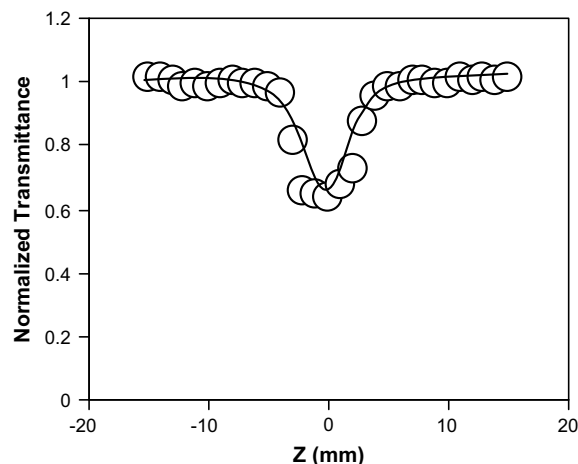


Fig. 3. Normalized transmittance of SA1 sample using the open-aperture Z-scan scheme.

wavelength region 200–800 nm at room temperature using DMF solvent as the reference. The UV-vis absorption spectra of the dye molecules are shown in Fig. 2.

Linear refractive index values of the samples used for the experiment have been obtained using Mettler Toledo Refractometer at the experimental wavelength. To see the effect of acceptor on the nonlinear properties of the dyes, experiments have been done on the dye sample in which thiobarbituric acid is replaced by cyano group (SA3).

3. Results and discussion

The UV absorption spectra show that there is negligible single photon absorption at 532 nm wavelength indicating that our measurements fall into the category of nonresonant interactions.

In order to determine the sign of third-order susceptibility ($\chi^{(3)}$) and to investigate the relative contributions from its real and imaginary parts, Z-scan studies were conducted. Fig. 3 shows the experimental open-aperture (OA) Z-scan data and Fig. 4 exhibits pure nonlinear refraction curve for the styryl dye sample, SA1. Similar curves have been obtained for SA2 molecules under the same experimental conditions which have been shown in Figs. 5 and 6. As seen from Fig. 4, pure nonlinear refraction curve shows the

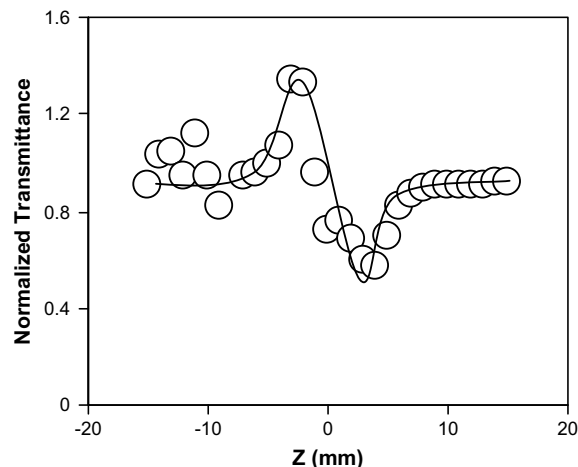


Fig. 4. Normalized transmittance of SA1 sample using the closed-aperture Z-scan scheme.

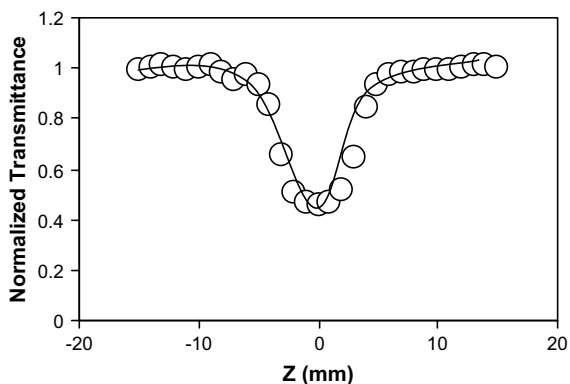


Fig. 5. Normalized transmittance of SA2 sample using the open-aperture Z-scan scheme.

prefocal transmittance peak followed by the postfocal valley which is the signature of negative nonlinearity. If the nonlinear transmissivity change is due to the pure TPA process, then the nonlinear absorption coefficient β should be independent of the input intensity I_0 [7]. However, if there are additional nonlinear absorption mechanisms such as excited state absorption or three-photon absorption, the apparently measured values of nonlinear absorption coefficient β will not remain constant [8–10]. One can see from Fig. 7 that the measured β values for the styryl dyes SA1 and SA2 are independent of the input intensity I_0 . Therefore, the major contribution to the observed nonlinear absorption is probably due to TPA process [11]. It is known that nonlinear absorption coefficient β depends on the number of absorptive centers in a unit volume. Assuming that this number is N_0 , in units of cm^{-3} , we have [12,13],

$$\beta = \sigma_2 N_0 = \sigma_2 N_A d \times 10^{-3} \quad (1)$$

Here, N_0 is the molecular density of the sample (in units of $1/\text{cm}^3$), σ_2 is the molecular TPA coefficient (or cross-section) (in units of cm^4/GW), d is the concentration of the colorant and N_A is the Avogadro number. For known β and d , the value of σ_2 can be obtained. In the literature [8,13], molecular TPA cross-section (in units of $\text{cm}^4 \text{ s}/\text{photon}$) is also defined as,

$$\sigma'_2 = \sigma_2 h\nu \quad (2)$$

where σ_2 is in units of $\text{cm}^4 \text{ s}$ and $h\nu$ is the energy (in joules) of an incident photon.

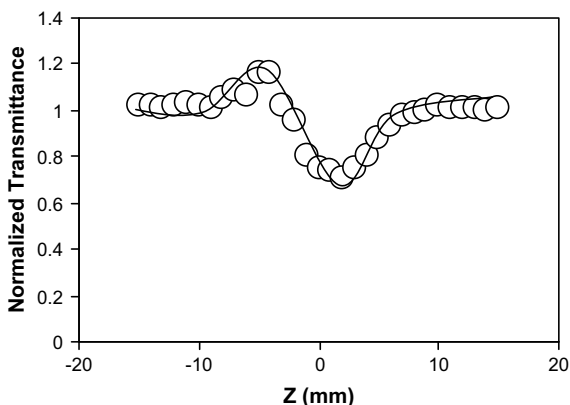


Fig. 6. Normalized transmittance of SA2 sample using the closed-aperture Z-scan scheme.

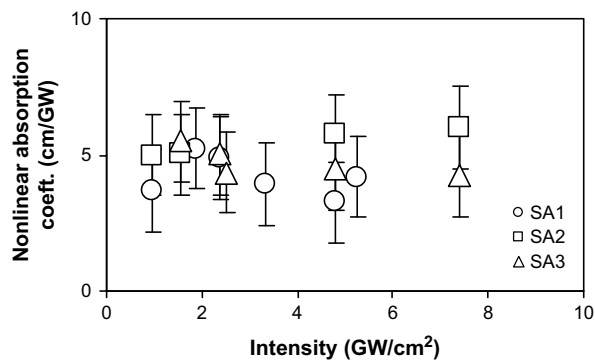


Fig. 7. Measured values of nonlinear absorption coefficient (β) of dye molecules at various input intensities.

The nonlinear refractive index n_2 is related to the real part of third-order nonlinear optical susceptibility through the equation [6],

$$\text{Re } \chi^{(3)} = 2n_0^2 c \epsilon_0 n_2 \quad (\text{esu}) \quad (3)$$

where n_0 is the linear refractive index, ϵ_0 is the permittivity of free space and c is velocity of light in vacuum.

Now the nonlinear absorption coefficient β is related to the imaginary part of third-order nonlinear optical susceptibility through the equation [6],

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

where n_0 is the linear refractive index, ϵ_0 is the permittivity of free space and c is velocity of light in vacuum.

From the Z-scan data, the real and imaginary parts of the $\chi^{(3)}$ have been calculated to be -3.0×10^{-13} esu and 0.76×10^{-13} esu for SA1 molecules. Nonlinear absorption coefficient is found to be $4.87 \text{ cm}^4/\text{GW}$, effective two-photon absorption cross-section is $1.72 \times 10^{-19} \text{ cm}^4/\text{GW}$. When the molecules of SA1 are attached with one more methoxy group at the 3-position (sample SA2), the real and imaginary parts of $\chi^{(3)}$ changed to -1.52×10^{-13} esu and 1.14×10^{-13} esu and excited state absorption cross-section increased to $2.8 \times 10^{-19} \text{ cm}^4/\text{GW}$.

The nonlinear response of our samples is attributed to the presence of methoxy group in the phenyl ring. It is a *p*-director and ring activator. Apart from the electron pumping effect, the methoxy group attached to the conjugate system is known to exhibit a special type of resonance called hyperconjugative or no bond resonance. Hence the electron density of the phenyl ring is enhanced. As a result, there is a greater donation of π electrons from the donor to the 1,3-diethyl-2-thioxodihydropyrimidine acceptor [14,15]. The donor–acceptor strengths and conjugated

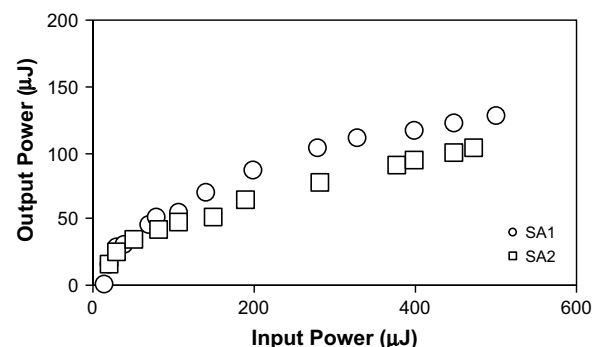


Fig. 8. Optical power limiting behavior of styryl dyes.

Table 1Third-order nonlinear coefficients of styryl dyes at 532 nm. Solvent used is DMF. Concentration of the solution 4.3×10^{-2} mol/L.

Sample	n_2 (10^{-14} cm ² /W)	Re $\chi^{(3)}$ (10^{-13} esu)	Im $\chi^{(3)}$ (10^{-13} esu)	β (cm/GW)	σ_2 (10^{-19} cm ⁴ /GW)	Coupling factor (ρ)
SA1	-7.57	-3.0	0.76	4.87	1.72	0.27
SA2	-4.15	-1.52	1.14	7.31	2.80	0.75
SA3	-6.03	-2.23	0.76	5.01	1.36	0.35

bridge length have a strong impact on the absorption cross-section [16,17]. It is due to this reason that, the absorption cross-section is higher for SA2 molecules.

Fig. 8 shows the optical power limiting behavior of the molecules at 532 nm. The limiting threshold of SA1 and SA2 samples was 70 μ J and 52 μ J, respectively. The difference in the saturation level of the output power is due to the difference in conjugation length and the strength of the acceptor/donor end groups in the two compounds [18]. Since the third-order nonlinear response arises due to delocalisation of the electron, the power limiting is ascribed to the two-photon absorption mechanism.

With the same acceptor group when the donor, 4-methoxybenzylidene, is replaced with 3,4-dimethoxybenzylidene i.e., with two methoxy group attached to the donor group, nonlinear absorption is increased because of the increase in electron density. But when the acceptor group, thiobarbituric acid, is replaced by cyano group due to increased conjugation length, nonlinear refraction parameters have been increased and values have been tabulated in Table 1.

4. Conclusion

The third-order nonlinear optical parameters of two newly synthesized conjugated styryl dyes in pure form have been investigated by Z-scan technique using 7 ns laser pulses at 532 nm. The results demonstrate that the molecules possess negative nonlinearity due to the presence of methoxy group in the phenyl ring. Two-photon absorption mechanism plays a major role in the observed nonlinearity and the absorption parameters depend on the strength of the donor group. It is also found that the increased electron density enhances the nonlinear absorption and increased conjugation length increases the nonlinear refraction part.

The two-photon absorption cross-section values are about two orders of magnitude larger than those of commercially available azoaromatic compounds, because of relatively large nonresonant third-order nonlinear optical parameters.

Our investigations on the optical power limiting capability of the two compounds indicate that they are very promising nonlinear optical materials for power limiting applications.

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