Optical Materials 34 (2012) 1751–1757

Contents lists available at SciVerse ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Third order optical nonlinearity and optical limiting studies of propane hydrazides

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ARTICLE INFO

Article history:
Received 9 December 2011
Received in revised form 6 April 2012
Accepted 7 April 2012
Available online 23 May 2012

Keywords:
Non-linear optical properties
Z-scan
Optical limiting
Two photon absorption

ABSTRACT

Four hydrazones, 2-(4-isobutylphenyl)-N′-[phenylmethylene] propanehydrazide (P_1), 2-(4-isobutylphenyl)-N′-[(4- tolyl)methylene] propane hydrazide (P_2), 2-(4-isobutylphenyl)-N′-[1-(4- chlorophenyl)ethylidene] propanehydrazide (P_3) and 2-(4-isobutylphenyl)-N′-[1-(4-Nitrrophenyl)ethylidene] propane hydrazide (P_4) were synthesized and their third order nonlinear optical properties have been investigated using a single beam Z-scan technique with nanosecond laser pulses at 532 nm. The measurement on the compound-P_1 is not reported as there is no detectable nonlinear response. Open aperture data of the other three compounds indicate two photon absorption at this wavelength. The nonlinear refractive index n_2, nonlinear absorption coefficient β, magnitude of effective third order susceptibility $\chi^{(3)}$, the second order hyperpolarizability γ_h and the coupling factor ρ have been estimated. The values obtained are comparable with the values obtained for 4-methoxy chalcone derivatives and dibenzylideneacetone derivatives. The experimentally determined values of β, n_2, Re $\chi^{(3)}$ and Im $\chi^{(3)}$, γ_h and ρ of the compound-P_4 are 1.42 cm/GW, -0.619×10^{-11} esu, -0.663×10^{-13} esu, 0.22×10^{-13} esu, 0.34×10^{-32} esu and 0.33 respectively. Further the compound-P_4 exhibited the best optical power limiting behavior at 532 nm among the compounds studied. Our studies suggest that compounds P_2, P_3 and P_4 are potential candidates for the optical device applications such as optical limiters and optical switches.

1. Introduction

The interaction between materials and intense electromagnetic fields from high power laser pulses modulates the parameters of the laser pulse itself, which is referred to as nonlinear optical effect [1–4]. Materials possessing such nonlinear optical response can be exploited for the manipulation of optical signals in a variety of optical devices. NLO materials possessing the required properties for specific applications continue to be a topic of research in spite of extensive investigations carried out in the past on a large variety of materials such as semiconductors [2], conjugated organic polymers [3], porphyrins [3], liquid crystals [4], dyes [5,6], fullerenes [7], nanocomposites [8], charge transfer complexes [9] and organometallics [10].

The phenomenon of optical power limiting, a nonlinear optical effect, has attracted much attention due to its application to protection of eyes and sensitive optical devices from high power laser pulses. Since the discovery of optical limiting phenomenon, much work has been done in synthesizing new materials with adequate optical limiting property.

An optical limiter strongly attenuates the laser pulses of high intensity where as it is completely transparent at lower light intensities. Ideally, the laser pulse energy transmitted through the limiter rises linearly with input energy and saturates to a constant value at high energies. The limiting threshold is defined as the input energy at which the transmittance is fifty percent. Above the threshold, the output energy is clamped to the saturated value which depends on the material [11].

The origin of the nonlinear optical susceptibilities of organic compounds is not only electronic, but also ionic [12]. Generally, optical limiting property exhibited by organic molecules is related to high delocalization of the pi-electrons. The optical limiting behavior resulting from nonlinear absorption can occur due to reverse saturable absorption, two photon absorption, nonlinear refraction and nonlinear scattering. Nonlinear optical property observed in some materials such as semiconductor can be explained on the basis of two photon absorption wherein the material absorbs two photons simultaneously at the higher light intensity [13].

In general, the method adopted to improve the nonlinear optical properties is to synthesize organic compounds of the type, electron donor–bridge–electron acceptor/donor (D–bridge–A or D–bridge–D). The molecules in which donor and acceptor groups connected at the terminal positions of a pi bridge to create highly polarized

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http://dx.doi.org/10.1016/j.optmat.2012.04.011

molecules could exhibit large molecular nonlinearity. A series of compounds with different donor and acceptor groups at the terminal positions of a hydrazone bridge have been synthesized. The experimental investigation of the third order nonlinear optical susceptibility in the synthesized compounds, 2-(4-isobutylphenyl) -N′-[phenylmethylene] propanehydrazide (P_1), 2-(4-isobutylphenyl)-N′-[(4-ethylphenyl) methylene] propane hydrazide (P_2), 2-(4-isobutylphenyl)-N′-[1-(4-chlorophenyl)ethylidene] propanehydrazide (P_3) and 2-(4-isobutylphenyl)-N′-[1-(4-Nitrophenyl) ethylidene] propane hydrazide (P_4) dissolved in dimethyl formamide (DMF) with the single beam Z-scan technique with nanosecond laser pulses at 532 nm have been reported. We also discuss the influence of donor/acceptor groups on the third order nonlinear optical properties of these molecules. The measurement on the compound P_1 is not reported as there is no detectable nonlinear response.

2. Materials and methods

2.1. Synthesis and characterization

P_1, $C_{20}H_{24}N_2O$, was obtained by refluxing 2-[4-(2-methylpropyl) phenyl] propanehydrazide and benzaldehyde in ethanol in presence of few drops of concentrated sulfuric acid for 1 h. Excess ethanol was removed from the reaction mixture under reduced pressure. The solid product obtained was filtered, washed with ethanol and dried.

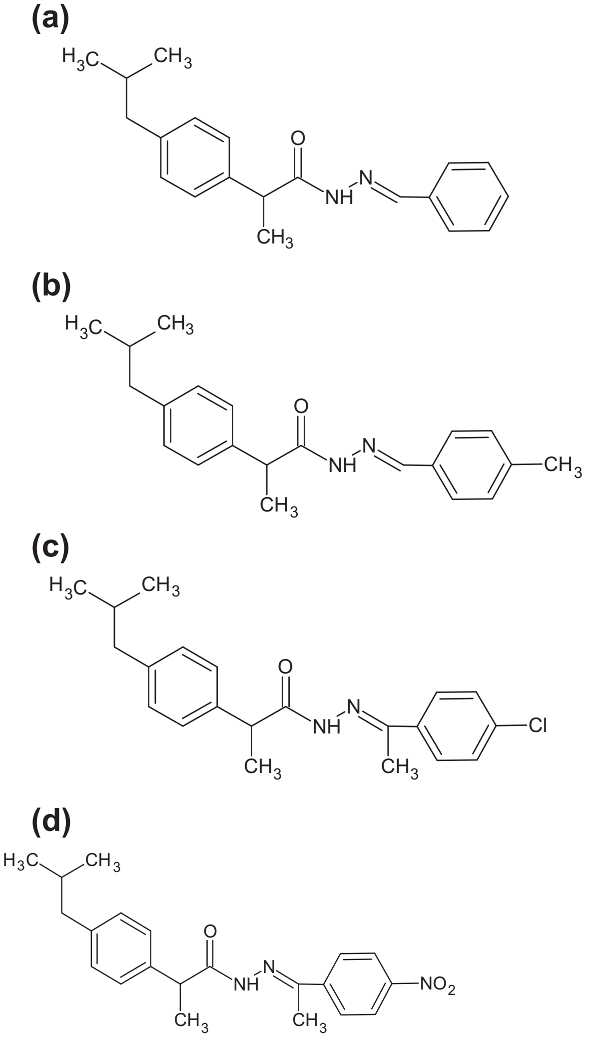

Fig. 1. Structure of compounds (a) P_1, (b) P_2, (c) P_3 and (d) P_4.

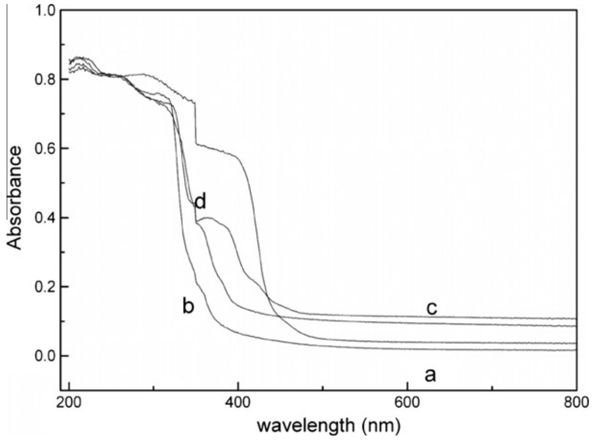

Fig. 2. UV–visible spectra of propane hydrazides (a) P_1, (b) P_2, (c) P_3 and (d) P_4.

P_2, $C_{20}H_{24}N_2O$, was obtained by refluxing 2-[4-(2-methylpropyl)phenyl] propanehydrazide and tolualdehyde in ethanol in presence of few drops of concentrated sulfuric acid for 1 h. Excess ethanol was removed from the reaction mixture under reduced pressure. The solid product obtained was filtered, washed with ethanol and dried.

P_3, $C_{21}H_{25}N_2OCl$, was obtained by refluxing 2-[4-(2-methylpropyl)phenyl] propanehydrazide and 4-chloroacetophenone in ethanol in presence of few drops of concentrated sulfuric acid for 1 h. Excess ethanol was removed from the reaction mixture under reduced pressure. The solid product obtained was filtered, washed with ethanol and dried.

P_4, $C_{21}H_{25}N_3O_3$, was obtained by refluxing 2-[4-(2-methylpropyl) phenyl] propanehydrazide and 4-nitroacetophenone in ethanol in presence of few drops of concentrated sulfuric acid for 1 h. Excess ethanol was removed from the reaction mixture under reduced pressure. The solid product obtained was filtered, washed with ethanol and dried. The molecular structures of the compounds are given in Fig. 1.

The linear refractive indices of these samples dissolved in DMF were measured using an Abbe refractometer. UV visible spectra were recorded using a SHIMADZU UV–VIS–NIR scanning spectrophotometer (model 3101 PC). There is no absorption of light in the visible region (Fig. 2). In the UV–visible spectra of propane hydrazides, below 350 nm, more than one peak are observed for the compounds P_1 (223, 253, 317 nm), P_2 (213, 287, 307 nm), P_3 (217, 257, 316, 370 nm) and P_4 (223, 292, 349 nm). The observed peaks are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. In the absorption spectra of the compounds, we can see a red shift in the cut-off wavelength as the conjugation increases in the order P_1 (376 nm) < P_2 (400 nm) < P_3 (445 nm) < P_4 (454 nm). The optical energy band gap for the compounds are found as 2.89 eV, 2.88 eV, 2.73 eV and 2.59 eV for the compounds P_1, P_2, P_3 and P_4 respectively. The compound P_4, which contains more polar group NO_2 compared to other compounds, is more conjugated and more delocalized and has minimum optical energy band gap.

2.2. Transmission measurements

The third order optical nonlinearity was investigated by the Z-scan technique which has become a popular method for the measurement of optical nonlinearities of materials. It not only has the advantages of simplicity and high sensitivity, but also enables simultaneous measurement of the magnitude and sign of the nonlinear refractive index and the nonlinear absorption coefficient of the samples [14]. Basically, the method consists of translating a sample through the focus of a Gaussian beam and monitoring the changes in the far field intensity pattern. When the intensity of the incident laser beam is sufficient to induce nonlinearity in the sample, it either converges (self focusing) or diverges (self defocusing) the beam, depending on the nature of that nonlinearity. By moving the sample through the focus, the intensity dependent absorption is measured as a change of transmittance through the sample (open aperture). The nonlinear refraction is determined by the intensity variation at the plane of a finite aperture placed in front of the detector (closed aperture), because the sample itself acts as a thin lens with varying focal length as it moves through the focal plane.

A *Q*-switched Nd: YAG nanosecond laser with a pulse width of 8 ns at 532 nm and a pulse repetition rate of 10 Hz was used as a source of light in our experiment. The output of the laser beam had a nearly Gaussian intensity profile. Solutions of the compounds in dimethyl formamide (DMF) were prepared and the concentration of the solution was 1×10^{-2} mol/L. The Gaussian laser beam was focused by using a lens of focal length 25 cm, into the sample solution contained in a 1 mm quartz cuvette. The resulting beam waist radius at the focus was calculated using the formula, $\omega_0 = 1.22\, f\, \lambda/d$, where '*f*' is the focal length of the lens and '*d*' the diameter of the aperture. It was found to be 18.9 μm. The corresponding Rayleigh length, calculated using the formula $Z_R = \pi\omega_0^2/\lambda$, was found to be 2.11 mm. The sample thickness of 1 mm was less than the Rayleigh length and hence it could be treated as a 'thin medium'. The Z-scan was performed at laser pulse energy of 200 μJ, which resulted in an on-axis peak irradiance of 4.78 GW/cm^2. The measurements were done at room temperature. The optical limiting measurements were carried out keeping the sample at the focal point and varying the input energy and recording the output energy without placing an aperture in front of the detector. Two pyroelectric detectors along with the Laser Probe Rj-7620 energy meter were used to record the incident and the transmitted energies simultaneously. In order to avoid cumulative thermal effect, the data were collected in a single shot mode [15]. Further to determine the contribution of the solvent to nonlinear refractive index (n_2), we conducted Z-scan experiment on pure DMF and found that it showed neither nonlinear refraction nor nonlinear absorption. Hence the contribution of the solvent to the nonlinearity of the sample is taken to be negligible.

The nonlinear transmission of compounds with and without an aperture placed in front of the detector were measured in the far field as the sample was moved through the focal point. This allows us to separate the nonlinear refraction from the nonlinear absorption. In the open aperture curve which shows the normalized transmission without an aperture at 532 nm, the curves are nearly symmetric with respect to the focus ($Z = 0$), where it has a minimum transmission, showing an intensity dependent absorption effect. This may include nonlinear optical processes like two photon absorption (TPA), excited state absorption (ESA), free carrier absorption and reverse saturable absorption. Nonlinear absorption under nanosecond excitation can be explained using the five level energy diagram [16–18] as shown in Fig. 3. Ground state S_0, the first singlet state S_1, the next higher excited singlet state S_2, lower triplet state T_1 and next higher triplet state T_2 form the different levels. When two photons of the same or different energy are simultaneously absorbed from the ground state to a higher excited state ($S_1 \leftarrow S_0$), it is denoted as two-photon absorption. When excited state absorption occurs, molecules are excited from an already excited state to a higher excited state ($S_2 \leftarrow S_1$ or $T_2 \leftarrow T_1$). The population of the excited state (S_1 or T_1) needs to be high so that the probability of photon absorption from that state is high. In nanosecond timescale, singlet transition does not deplete the population of S_1 level appreciably, since atoms excited to S_2 decay to S_1 itself with in picoseconds. From S_1, electrons are transferred to T_1 via intersystem crossing (ISC), from where transitions to T_2 occur. If more absorption occurs from the excited state than from the ground state, it is usually called reverse saturable absorption. The triplet excited state absorption may result in RSA if the absorption cross section of triplet excited state is greater than that of singlet excited state. With excitation of laser pulses on the nanosecond scale, which is true in our case, triplet–triplet transitions are expected to make significant contribution to nonlinear absorption.

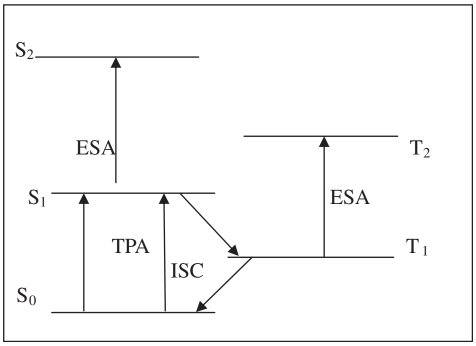

Fig. 3. Energy level diagram showing both two-photon absorption and excited state absorption (five level models).

The model described in [14] was used to determine the magnitude of nonlinear absorption coefficient (β) and the third order susceptibility $\chi^{(3)}$ of the samples. The nonlinear absorption coefficient was determined using the Eq. (1), since the laser beam has nearly a Gaussian transverse intensity distribution. The normalized transmittance for the open aperture Z-scan is given by Sheik-Bahae et al. [14].

In order to extract the information on nonlinear refraction, the sample is moved through the focal point and the nonlinear transmission was measured as a function of sample position with an aperture placed infront of the detector. In almost all materials, the nonlinear refraction (NLR) is accompanied by the nonlinear absorption (NLA). Thus, in the case of materials having negative refractive nonlinearity, the transmittance curve for the closed aperture Z-scan should have a smaller peak and a larger valley. To obtain a pure nonlinear refraction curve, we have used the division method described in [14]. The peak and valley configuration of the curve thus obtained by dividing closed aperture curve by open aperture curve clearly indicates that the material has a negative nonlinear refractive index. The response is electronic in origin and the thermal effect is not the dominant effect for the third order nonlinear response of the solution. The difference between the peak and valley ($\Delta Tp{-}v$) in the pure nonlinear refraction (NLR) curve is used to calculate the nonlinear refractive index (γ) of the compounds using the relation

$$\gamma = \Delta\phi_o \lambda / 2\pi L_{\text{eff}} I_0 \ (\text{m}^2/\text{W}) \tag{1}$$

where λ is the wavelength of the laser light and $\Delta\varphi_0$ is the nonlinear phase shift given by the relation

$$|\Delta\phi_0| = \Delta Tp - v/0.406(1-S)^{0.25} \quad for|\Delta\phi_0| \le \pi \tag{2}$$

where *S* (50%) is the aperture linear transmittance.

The real and imaginary parts of the third order nonlinear susceptibility can be calculated using the relations

$$\chi_R^{(3)} = 2n_0^2 \varepsilon_0 c\gamma \tag{3}$$

$$\chi_I^{(3)} = n_0^2 \varepsilon_0 c^2 \beta/\omega \tag{4}$$

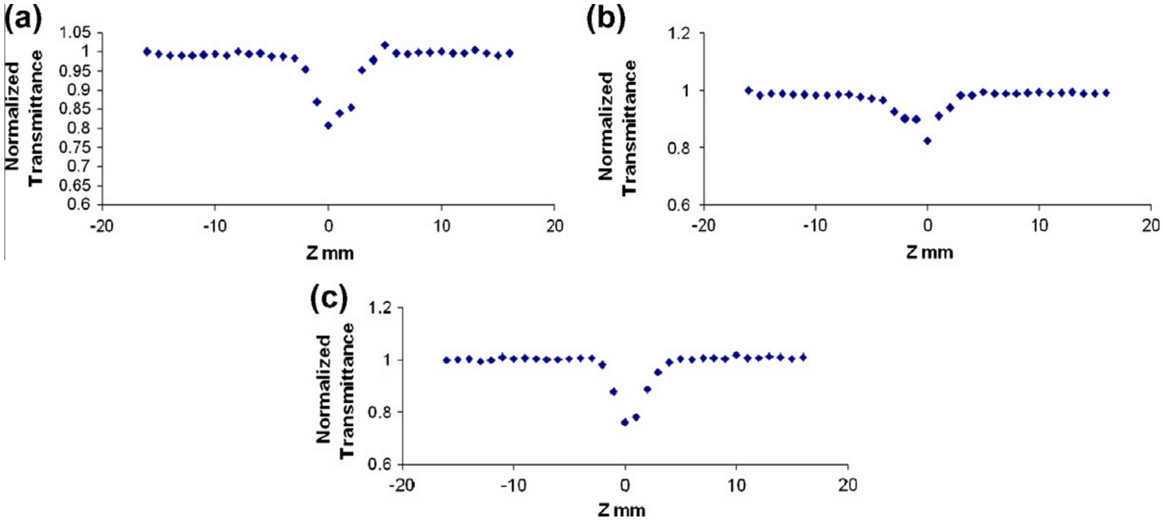

Fig. 4. Open aperture Z-scan curves of propane hydrazides (a) P_2, (b) P_3 and (c) P_4.

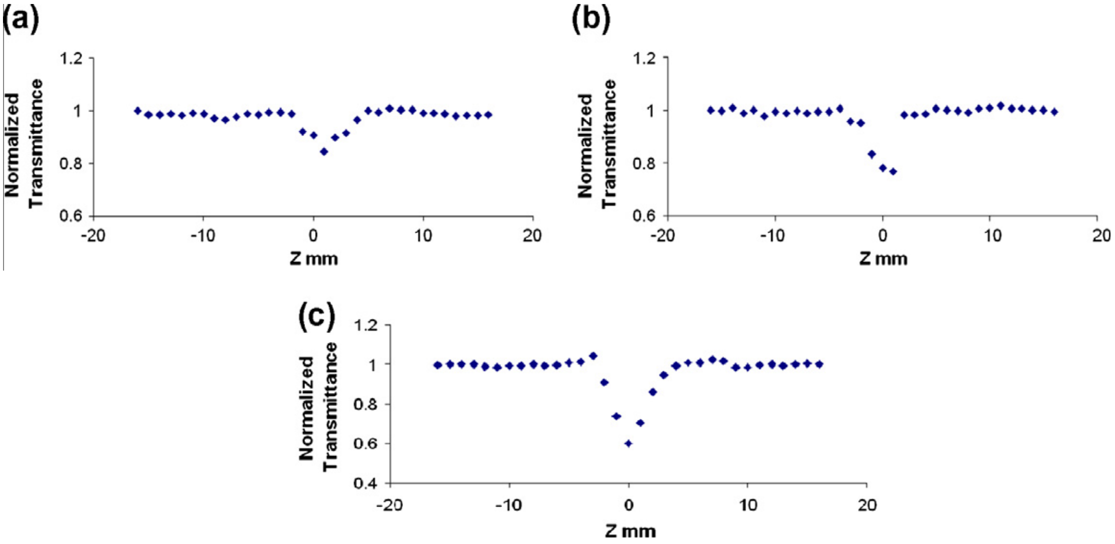

Fig. 5. Closed aperture Z-scan curves of propane hydrazides (a) P_2, (b) P_3 and (c) P_4.

where n_0 is the linear refractive index, ε_0 is the permittivity of free space and c is the velocity of light in vacuum. The nonlinear refractive index n_2 (in esu) can be obtained by the conversion formula

$$n_2 = (cn_0/40\pi)\gamma \text{ esu} \tag{5}$$

The second order hyperpolarizability $\boldsymbol{\gamma_h}$ of a molecule in an isotropic medium is related to the macroscopic third order susceptibility as given by Gunter [19].

The coupling factor ρ is the ratio of imaginary part to real part of third order nonlinear susceptibility, i.e.:

$$P = \text{Im } \chi^{(3)}/\text{Re } \chi^{(3)} \tag{6}$$

It is known that the nonlinear absorption coefficient β depends on the number of absorptive centers in a unit volume [20,21].

Further, the molecular TPA cross section can also be expressed as

$$\sigma_2^1 = \sigma_2 \; h\upsilon \tag{7}$$

where σ_2^1 is in units of cm^4 s and $h\nu$ is the energy (in joules) of an incident photon.

The values of effective excited state absorption cross-section of the compounds are found from the relation $\sigma_{ex} = q_0F_0 \, L_{eff}/h\upsilon$ where F_0 is the on-axis fluence at the focus, which is related to the incident energy as $F_0 = E_{total}/\pi\omega_0^2$. The ground state absorption was calculated using the relation $\sigma_g = \alpha/N_A \, C$ where N_A is the Avogadro number and C the concentration in mol/L.

3. Results and discussion

We have synthesized a series of compounds with hydrazone bridge and different donor and acceptor groups. In compounds (P_1–P_4), hydrazone acts as a pi bridge for pi electron delocalization across the donor–acceptor links. Change in donor/acceptor groups leads to large nonlinearities. The synthesized molecules possesses donor–acceptor–acceptor (D–A–A) and donor–acceptor–donor (D–A–D) type structures. Compounds P_1 and P_2 are D–A–D type compounds in which isobutyl phenyl group attached at one end acts as a donor, the oxygen of the carbonyl group in the center acts as an acceptor and phenyl/methyl phenyl group attached to the other end acts as electron donor. Compounds P_3 and P_4 are D–A–A type in which isobutyl phenyl group attached at one end acts as a donor,

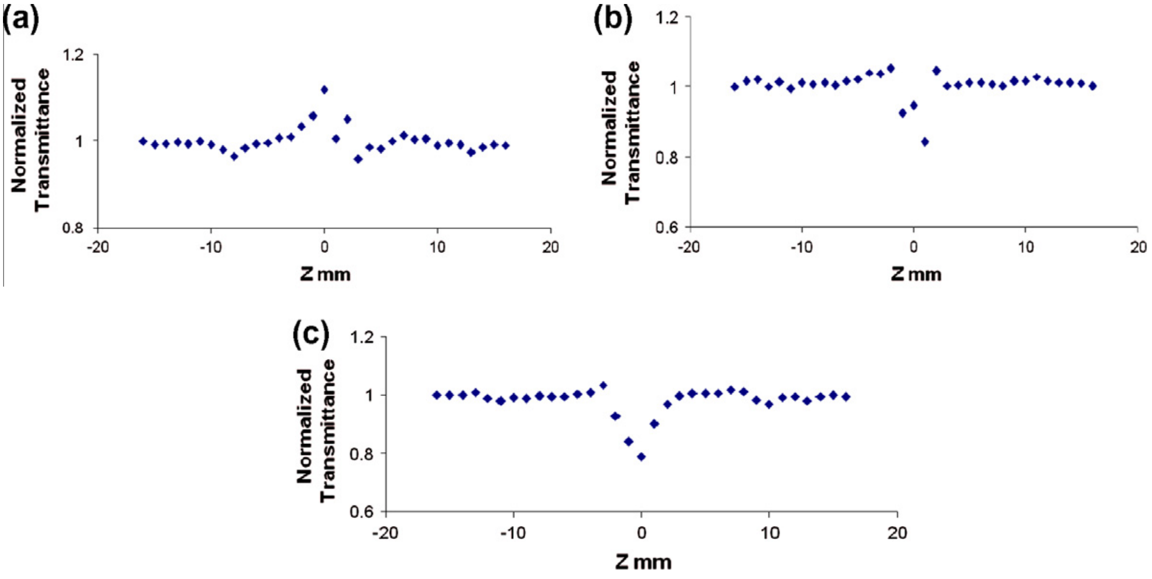

Fig. 6. Nonlinear refraction curves of propane hydrazides (a) P_2, (b) P_3 and (c) P_4.

the oxygen of the carbonyl group in the center and chlorophenyl/nitro phenyl group attached to the other end of the molecule acts as an acceptor. The model described in [14] was used to determine the magnitude of nonlinear absorption coefficient (β) and the third order susceptibility $\chi^{(3)}$ of the samples.

In the derivatives of propane hydrazides, compounds P_1 and P_2 are D–pi–D type compounds in which isobutyl phenyl group attached at one end acts as a donor and phenyl/methylphenyl group attached to the other end acts as electron donor. Compounds P_3 and P_4 are D–pi–A type in which isobutyl phenyl group attached at one end acts as a donor and chloro phenyl/nitro phenyl group attached to the other end of the molecule acts as an acceptor. The open aperture Z-scan traces of the compounds obtained by performing the open aperture Z-scan experiment are given in Fig. 4. The magnitude of nonlinear absorption coefficient β is calculated from the open aperture Z-scan traces.

Closed aperture Z-scan was performed to determine the sign and magnitude of nonlinear refraction. The peak-valley configuration of the pure nonlinear refraction curves for the studied compounds clearly demonstrate that the index change is negative (Fig. 5), exhibiting defocusing effect.

In order to extract the pure nonlinear refraction part, we have divided the value of the closed aperture data by the open aperture data. Fig. 6 shows the resulting curve corresponding to pure nonlinear refraction. The difference between the peak and valley in the pure nonlinear refraction curve is used to calculate the nonlinear refractive index of the compounds.

The open aperture, closed aperture and nonlinear refraction curves of derivatives of propane hydrazides are shown in Figs. 4–6 respectively.

The experimentally determined values of β, n_2, Re $\chi^{(3)}$ and Im $\chi^{(3)}$ of the compounds are given in Table 1. The measurement on the compound-P_1 is not reported as there is no detectable nonlinear response. The values of Re $\chi^{(3)}$ of the compounds increase in the order compound-P_4 > compound-P_3 > compound-P_2. The value of Re $\chi^{(3)}$ for compound-P_4 is 0.66×10^{-13} esu, which shows that the Re $\chi^{(3)}$ of compound-P_4 is nearly double compared to that the Re $\chi^{(3)}$ value of compound-P_2 (0.36×10^{-13}). The nitro group in compound-P_4 is a strong electron acceptor compared to chlorine in compound-P_3 and methyl phenyl group in compound-P_2. Hence the charge transfer is more effective in compound-P_4, leading to higher nonlinear response compared to compound-P_3. Chlorine being a stronger acceptor than methyl phenyl group, the charge transfer is more effective in compound-P_3 than compound-P_2.

Table 1
Experimentally determined values of nonlinear optical parameters.

Compounds	n_0	n_2 (esu)	β (cm/GW)	Re $\chi^{(3)}$ (esu)	Im $\chi^{(3)}$ (esu)
P_2	1.420	-0.9×10^{-11}	1.12	-0.36×10^{-13}	0.17×10^{-13}
P_3	1.417	-1.3×10^{-11}	1.03	-0.47×10^{-13}	0.16×10^{-13}
P_4	1.419	-1.8×10^{-11}	1.42	-0.66×10^{-13}	0.22×10^{-13}

Delocalization also enhances the second order hyperpolarizability of the molecule. The macroscopic susceptibility of third order is linearly related to the microscopic second order hyperpolarizability. The second order hyperpolarizability $\boldsymbol{\gamma_h}$ of a molecule in an isotropic medium is related to the third order susceptibility by the relation 7. The microscopic second order hyperpolarizabilities of the compounds are given in Table 2. The values can be compared with the values of organic molecules and polymers reported in the literature. The $\boldsymbol{\gamma_h}$ values obtained in the present investigation are comparable with the values reported for 4-methoxy chalcone derivatives, reported by Ravindra et al. [22], with that of thiophene (hexamer) [23], with copolymers by John Kiran et al. [24] and with chalcone derivatives in polymer host, reported by Shettigar et al. [25]. These values are found to be greater than that of thiophene (dimer, trimer, tetra and pentamers) [23].

The observed values of the coupling factor ρ using the relation 8 for all the compounds are around 1/3, indicating that the nonlinearity is electronic in origin. The dependence of $\chi^{(3)}$ on donor/acceptor type substituents in these compounds clearly show that the nonlinearity is of electronic origin and the thermal effect does

Table 2
Experimentally determined values of the nonlinear optical parameters.

Compounds	$\Delta\varphi_0$	γ_h (esu)	σ_2^1 (cm^4 s/photon)	ρ
P_2	0.56	0.19×10^{-32}	0.70×10^{-46}	0.48
P_3	0.74	0.25×10^{-32}	0.65×10^{-46}	0.33
P_4	1.03	0.34×10^{-32}	0.88×10^{-46}	0.33

not play any dominant role in the third order nonlinear response of the compounds.

From the nonlinear absorption coefficient β, the molecular TPA cross section σ_2^1 has been found out using the relations 9 and 10. The values are given in Table 2. It is found that the effective TPA cross-section of the compounds are of the order of 10^{-46} cm^4 s/photon, which are comparable with that for bis-chalcone derivatives in polymer host, reported by Shettigar et al. [26].

The nonlinear response of the compounds is mainly due to the enhanced pi–electron density in the molecule, chemical structure of the compound and on the electron accepting/donating ability of the groups present in the molecule. By the introduction of electron donors or acceptors, the electron density is enhanced. As a result, there is an increase in the magnitude of dipole moment which leads to large nonlinear susceptibilities. This shows that by increasing the donor/acceptor strength in hydrazone molecules, we can increase the third order nonlinear response. Hence through structure modification in this class of materials, one can achieve the nonlinear optical property. The pi electron delocalization and charge transfer contributes to the ultrafast optical response capability and large third order susceptibility.

The optical limiting experiment was conducted at 532 nm wavelength for all the compounds. Among the derivatives of propane hydrazides, the compound-P_4 shows better optical limiting at 532 nm wavelength (Fig. 7), compared to compounds P_2 and P_3. For a concentration of 1×10^{-2} mol/L, the output energy increases linearly with the incident energy up to input energies of 300 μJ/pulse. But for energies more than this, the output energy is almost constant assuming the value of 239 μJ/pulse.

For compound-P_4, when the concentration is increased to 2×10^{-2} mol/L, the output energy increases linearly with the increase in input energy, till 150 μJ/pulse. With further increase in the input energy, the output energy gets stabilized to nearly a constant value of 96 μJ/pulse. In the case of higher concentration (4×10^{-2} mol/L), the output energy increases linearly with the incident energy and for energies more than 150 μJ/pulse, the output energy is almost clamped around 84 μJ/pulse (Fig. 8).

It is seen that in the compound-P_4, the power limiting threshold decreases with increasing concentration. This is because at the higher concentration, there exists more molecules per unit volume; hence it absorbs the harsh laser pulses more efficiently. The variation in conjugation length and the presence of donor/acceptor end groups in the compounds also affect the limiting threshold. Higher conjugation length and stronger end groups can decrease the limiting threshold. Since the third order nonlinear response arises due to delocalization of electrons, the optical limiting is ascribed to the two photon absorption mechanism.

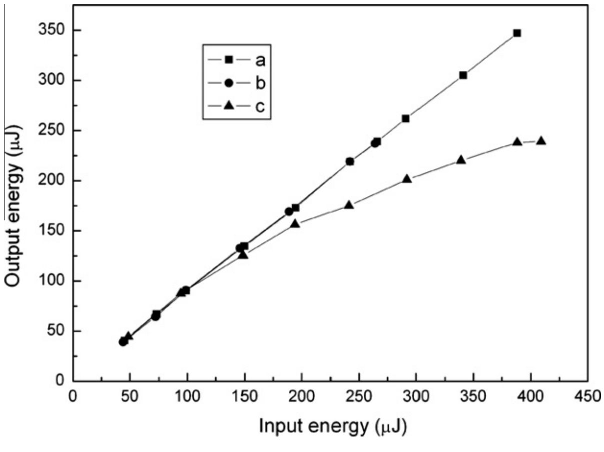

Fig. 7. Optical limiting of propane hydrazides (a) P_2, (b) P_3 and (c) P_4.

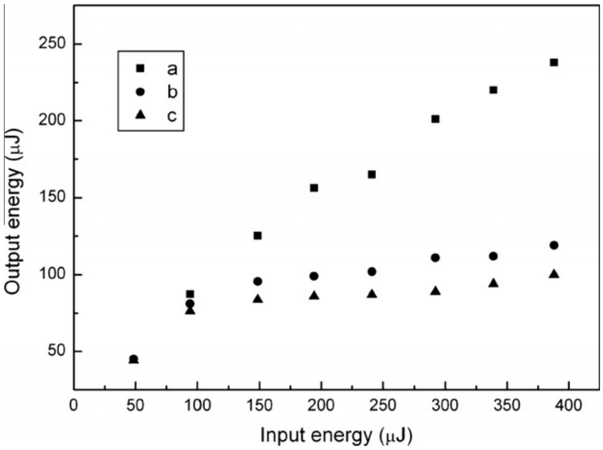

Fig. 8. Optical limiting of compound-P_4 for different concentrations. (a) 1×10^{-2} mol/L, (b) 2×10^{-2} mol/L and (c) 4×10^{-2} mol/L.

Table 3
Experimentally determined values of ground state and effective excited state absorption cross-sections.

Compounds	σ_{ex} (cm^2)	σ_g (cm^2)
P_2	1.132×10^{-19}	1.694×10^{-20}
P_3	1.041×10^{-19}	1.894×10^{-20}
P_4	1.427×10^{-19}	0.781×10^{-20}

The basic requirements for optical limiting applications, i.e. large nonlinear refraction and positive nonlinear absorption are observed in the reported compounds. It is confirmed by the presence of optical limiting. The large nonlinearities of the reported compounds are due to the delocalized electronic states [27]. The present result shows that the samples exhibit remarkable optical responses in the nanosecond domain, which help in designing organic materials suitable for optical limiters and optical switches.

The excited state absorption cross section was measured from the normalized open aperture Z-scan data. The measured values of ground state and effective excited state absorption cross-section of the compounds are given in Table 3.

The larger values of excited state cross section σ_{ex} as compared to ground state absorption cross section σ_g, indicates that the major nonlinear process causing the limiting behavior is reverse saturable absorption [28–30]. The obtained values of excited state and ground state absorption cross sections of the compounds are less than the values obtained for organometallic phthalocyanine [29] and thiophene based conjugated polymer [31] and comparable with the values of benzohydrazone derivatives reported by Vijayakumar et al. [32]. A smaller linear absorption at 532 nm and the measured σ_{ex} values indicate that there is a contribution from excited absorption to the observed nonlinear absorption. Materials that exhibit reverse saturable absorption (RSA) usually show good optical limiting characteristics of the high intensity laser pulses. Inorder to observe RSA, the excited state absorption cross section should be higher than that of the ground state absorption cross section and is consistent with the present result. Therefore, in these compounds, the two photon assisted excited state absorption leading to reverse saturable absorption may be responsible for the optical limiting action.

4. Conclusions

The derivatives propane hydrazones were synthesized and their third order nonlinear optical properties were investigated using a single beam Z-scan technique in the nanosecond domain at 532 nm. The base compound hydrazine does not show any significant nonlinearity. Open aperture data of the compounds demonstrate the occurrence of two photon absorption at this wavelength. The nonlinear refractive index, nonlinear absorption coefficient and the magnitude of effective third order nonlinear susceptibility have been estimated. The compounds with strong electron donating/accepting group exhibit good nonlinear optical response. The nonlinear refractive index, the third order nonlinear susceptibility, the molecular second order hyperpolarizability and the effective TPA coefficient of the compounds are of the order of 10^{-11}, 10^{-13}, 10^{-32} and 10^{-46} esu respectively. The values obtained are comparable with the values obtained for 4-methoxy chalcone derivatives and dibenzylidene acetone derivatives and better than the dmit organometallic complex BuCo and Cobalt doped Polyvinylpyrrolidone solution. In the propane hydrazide series, the compound-P_4 exhibits the best third order nonlinear optical susceptibility. The compounds show good optical limiting at 532 nm. The observed values of the coupling factor ρ for the molecules indicate the electronic origin of nonlinearity. These results suggest that the compounds may be used for the optical device applications such as optical limiters and optical switches. The present study reveals that the introduction of strong donor/acceptor groups leads to large nonlinearities and makes it possible to tailor the nonlinear optical property through structure modification in this class of materials.

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