



Synthesis, characterization and studies on the nonlinear optical parameters of hydrazones

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ABSTRACT

Three hydrazones, 2-(4-methylphenoxy)-*N'*-[(1*E*)-(4-nitrophenyl)methylene]acetohydrazide (compound-1), 2-(4-methylphenoxy)-*N'*-[(1*E*)-(4-methylphenyl)methylene]acetohydrazide (compound-2) and *N'*-[(1*E*)-[4-(dimethylamino)phenyl]methylene]-2-(4-ethylphenoxy) acetohydrazide (compound-3) were synthesized and their third order nonlinear optical properties were investigated using a single beam z-scan technique with nanosecond laser pulses at 532 nm. Open aperture data obtained from the three compounds indicates two photon absorption at this wavelength. The nonlinear refractive index n_2 , the nonlinear absorption coefficient β , the magnitude of the 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 dibenzylidene acetone derivatives. Among the compounds studied, compounds-1 and 3 exhibited the better optical power limiting behaviour at 532 nm. Our studies suggest that compounds-1, 2 and 3 are potential candidates for optical device applications such as optical limiters and optical switches.

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1. Introduction

In recent years, investigations into the nonlinear optical properties of different materials have attracted considerable attention, because they provide valuable information for the structural analysis of these materials and for their practical use in optoelectronic devices. Among a large number of materials with a pronounced nonlinear optical response, the compounds whose refractive indices change significantly with the intensity of light are of prime importance. This property provides a means of controlling the optical propagation in a medium. It is known that, for the most part, organic compounds with a strongly delocalized conjugate π -electron system possess the required property [1].

The design strategy, used by many with success, involves connecting donor and acceptor groups at the terminal position of a π bridge to create highly polarized molecules, which could exhibit large molecular nonlinearity. To date, the types of π bridges investigated for developing efficient NLO materials and molecules are D-Aolefines [2,3], acetylenes [4], azobridges [5], aromatic [6] and heteroaromatic rings [7,8].

Heterorings such as furan and thiophene, due to their relatively lower aromatic stabilization energy than benzene,

are reported to provide more effective π -conjugation between D and A, resulting in larger nonlinearities [9]. Various aromatic donors and acceptors have been used to tune electronic factor and understand the origin of nonlinearity in these molecules.

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

The optical limiting behaviour resulting from nonlinear absorption can occur due to reverse saturable absorption, two photon absorption, nonlinear refraction and nonlinear scattering. Nonlinear optical properties observed in some materials such as semiconductors can be explained on the basis of two photon absorption, wherein the material absorbs two photons simultaneously at higher light intensities [10].

Generally, optical limiting properties exhibited by organic molecules is related to high delocalization of the π -electrons. Excellent optical limiting responses have been reported in many phthalocyanines and their derivatives. They possess extensive two-dimensional π -electron delocalization and hence have been shown to be as promising NLO materials.

In general, the presence of strong nonlinear absorption is good for limiting property, while the presence of strong nonlinear refraction facilitates optical switching property of organic

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molecules. Organic compounds with large two photon absorption are good candidates for optical limiters (particularly for very short pulses) and highly efficient optical limiting performance has been demonstrated recently in stilbazolium salts [11].

In this paper, we report the synthesis and experimental investigation of the third order nonlinear optical properties in 2-(4-methylphenoxy)-*N*'-[(1*E*)-(4-nitrophenyl)methylene]acetohydrazide (compound-1), 2-(4-methylphenoxy)-*N*'-[(1*E*)-(4-methylphenyl)methylene]acetohydrazide ((compound-2) and *N*'-[(1*E*)-[4-(dimethylamino)phenyl)methylene]-2-(4-ethylphenoxy) acetohydrazide (compound-3) dissolved in dimethyl formamide (DMF) with the single beam z-scan technique with nanosecond laser pulses at 532 nm. We also discuss the influence of donor/acceptor groups on the third order nonlinear optical properties of these molecules.

2. Experiment

The three compounds were prepared by the acid catalysed condensation of *p*-tolylloxy acetahydrazide with appropriate aldehyde, i.e., 4-nitrobenzaldehyde, 4-methylbenzaldehyde and 4-(dimethylamino)benzaldehyde.

Compound-1, $C_{16}H_{15}N_3O_4$, was obtained by refluxing 2-(4-methylphenoxy)acetohydrazide (0.01 mol) and 4-nitrobenzaldehyde (0.01 mol) in ethanol (30 mL) by adding 2 drops of concentrated sulphuric 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. It was further purified by recrystallisation using ethanol.

Compound-2, $C_{17}H_{18}N_2O_2$, was obtained by refluxing 2-(4-methylphenoxy)acetohydrazide (0.01 mol) and 4-methylbenzaldehyde (0.01 mol) in ethanol (30 mL) by adding 2 drops of concentrated sulphuric 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 recrystallised using ethanol.

Compound-3, $C_{18}H_{21}N_3O_2$, was obtained by refluxing 2-(4-methylphenoxy)acetohydrazide (0.01 mol) and 4-(dimethylamino)benzaldehyde (0.01 mol) in ethanol (30 mL) by adding 2 drops of concentrated sulphuric 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 recrystallised using ethanol.

The structures of the compounds are given in Fig. 1. They are newly synthesized by the authors for the first time. The FTIR spectra are given in Fig. 2.

In compound-1, the C-H asymmetric stretching vibration occurs at 2960 cm^{-1} and N-H stretching vibration at 3097 cm^{-1} . The strong absorption band at 1697 cm^{-1} corresponds to C=O stretching vibration and C=C group appears at 1593 cm^{-1} . The medium absorption peaks at 1335 and 1518 cm^{-1} correspond to N=O (aromatic NO_2) symmetric-stretching and asymmetric-stretching vibrations, respectively.

In compound-2, the broad absorption band at 3461 cm^{-1} corresponds to the O-H stretching. The C-H asymmetric stretching vibration occurs at 2976 cm^{-1} and N-H stretching vibration at 3097 cm^{-1} . The strong absorption band at 1699 cm^{-1} corresponds to C=O stretching vibration and C=C group appears at 1531 cm^{-1} .

In compound-3, the C-H asymmetric stretching vibrations occur at 2900 cm^{-1} . The sharp peak at 3218 and 3066 cm^{-1} corresponds to N-H stretching and the broad absorption band at 3478 cm^{-1} corresponds to the O-H stretching. The strong absorption band at 1669 cm^{-1} indicates the presence of C=O stretching vibration and C=C group appears at 1593 cm^{-1} .

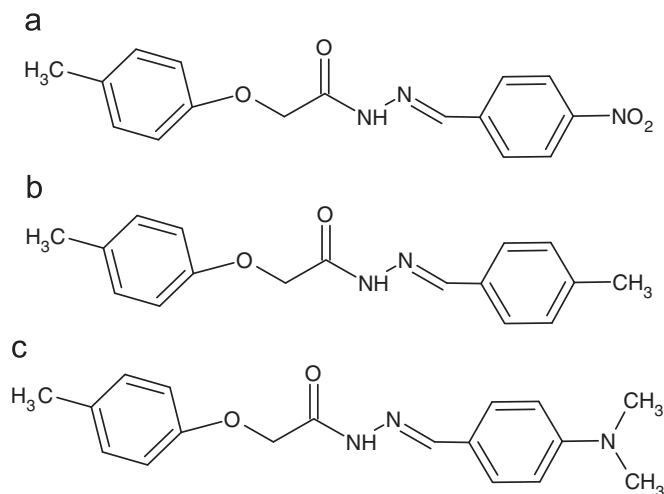


Fig. 1. Structures of the compounds: (a) Compound-1, (b) compound-2 and (c) compound-3.

To determine how the z-scan-measured transmittance is related to the nonlinear refraction of the sample, let us assume a medium with a negative nonlinear refractive index and a thickness smaller than the diffraction length of the focused beam. This can be considered as a thin lens of variable focal length. Beginning far from the focus ($z < 0$), the beam irradiance is low and nonlinear refraction is negligible. In this condition, the measured transmittance remains constant (i.e., z independent). As the sample approaches the beam focus, irradiance increases and leads to self-lensing in the sample. A negative self-lens before the focal plane will tend to collimate the beam on the aperture in the far field, increasing the transmittance measured at the iris position. After the focal plane, the same self-defocussing increases the beam divergence, leading to a widening of the beam at the iris and this reduces the measured transmittance. Far from the focus ($z > 0$), again the nonlinear refraction is low resulting in a transmittance z independent. A prefocal transmittance maximum (peak), followed by a post focal transmittance minimum (valley) is a z-scan signature of a negative nonlinearity. An inverse z-scan curve that is a valley followed by a peak characterizes a positive nonlinearity.

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 [12].

A Q-switched Nd:YAG nanosecond laser generating pulses at 532 nm was used as a source of light in our experiment. Solutions of the compounds in DMF were prepared and the concentration of the solution was 1×10^{-2} mol/L. A lens of focal length 26 cm was used to focus the laser beam into the sample solution contained in a 1 mm quartz cuvette. The resulting beam waist radius at the focus was $19.6\ \mu\text{m}$ that corresponds to the Rayleigh length of 2.274 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

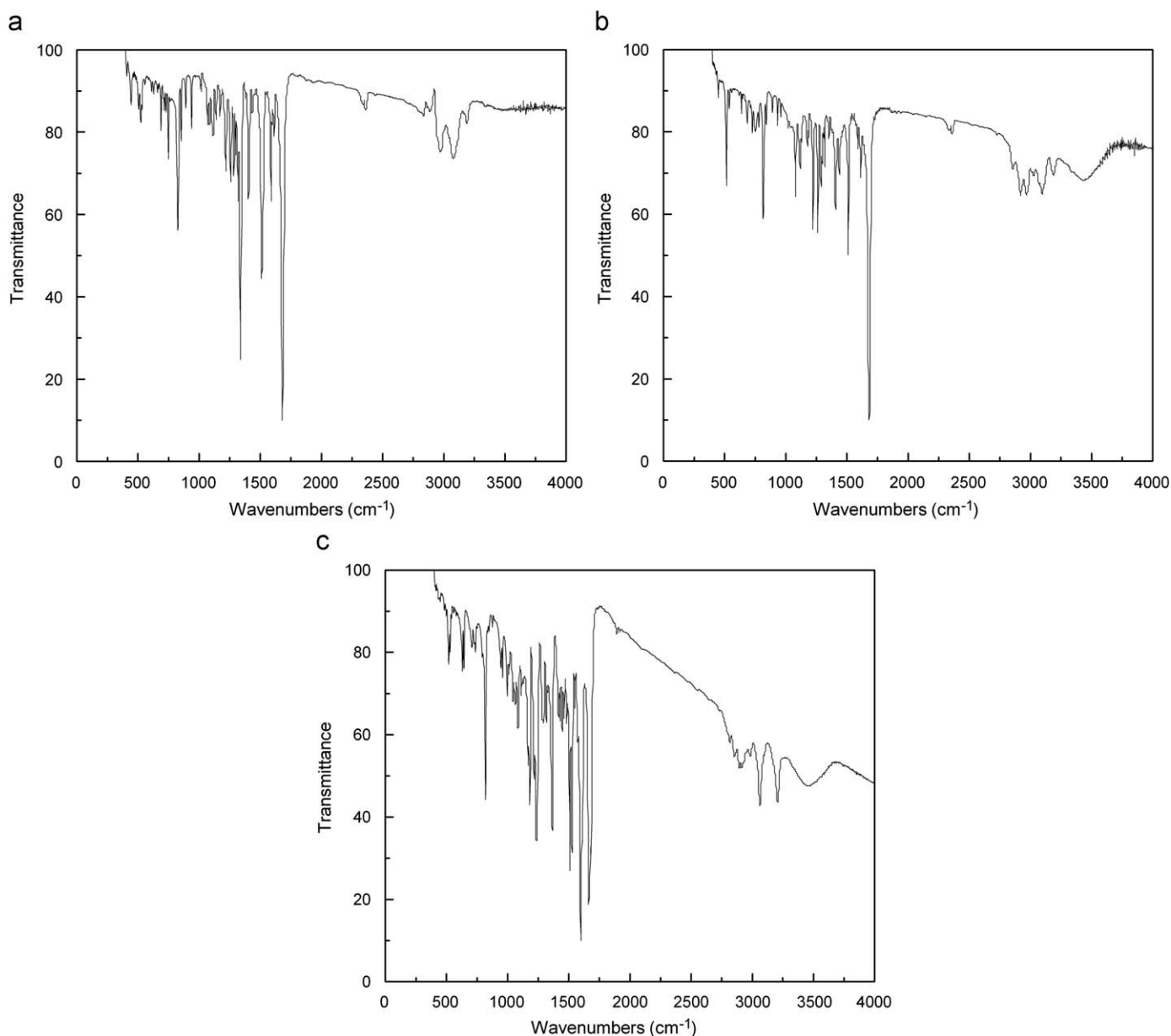


Fig. 2. FTIR spectra of the compounds: (a) Compound-1, (b) compound-2 and (c) compound-3.

transmitted energies simultaneously. 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. 3).

In the UV-visible spectra of the compounds, below 350 nm, a single peak is observed for compound-1 (327 nm), compound-2 (279 nm) and compound-3 (336 nm). The observed peak is assigned to $\pi \rightarrow \pi^*$ transition. According to the Valence Band theory, as the conjugation increases, the energy difference between the highest occupied and the lowest unoccupied π -orbitals decreases and hence the wavelength of the absorption band increases. 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 compound-2 (319 nm) < compound-3 (381 nm) < compound-1 (395 nm). The optical energy band gap for the compounds are found as 3.73, 3.30 and 3.07 eV for compounds-2, 3 and 1, respectively. Compound-1, which contains the more polar group NO_2 compared to other two compounds, is

more conjugated and more delocalized and has minimum optical energy band gap.

3. Results and discussion

One of the methods that has been adopted to improve the nonlinear optical properties of a material 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 are connected at the terminal positions of a π bridge to create highly polarized molecules could exhibit large molecular nonlinearity. In compounds (1–3), hydrazone acts as a π bridge for π electron delocalization across the donor-acceptor links. Changes in donor/acceptor groups leads to large nonlinearities. The synthesized molecules possess donor-acceptor-acceptor (D-A-A) and donor-acceptor-donor (D-A-D) type structures.

Compound-1 is a D-A-A type in which methylphenoxy group attached at one end acts as a donor, the oxygen of the carbonyl

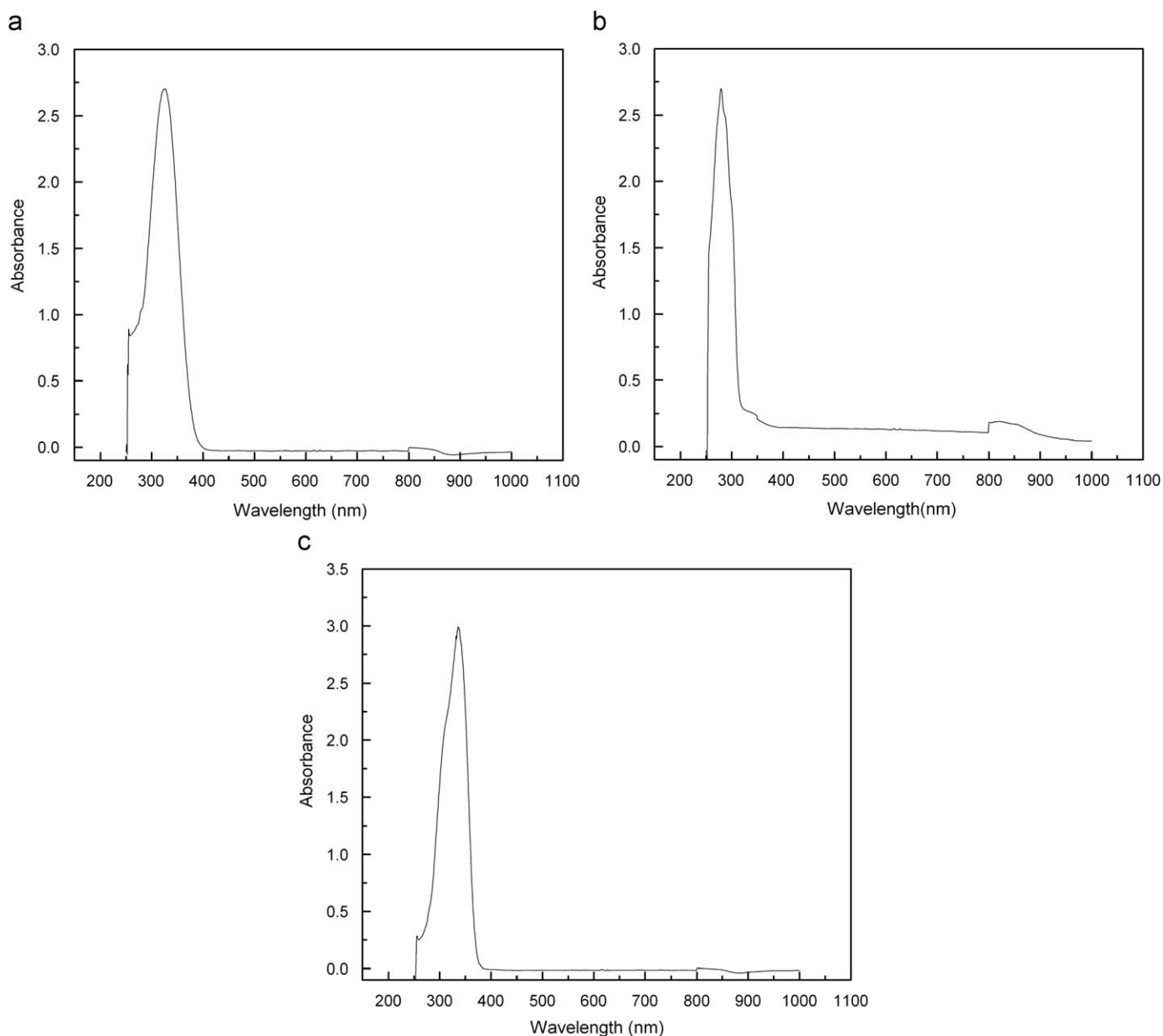


Fig. 3. Linear absorption spectra of the compounds: (a) Compound-1, (b) compound-2 and (c) compound-3.

group in the centre and nitro group attached to the other end of the molecule acts as an acceptor. Compounds-2 and 3 are D–A–D type compounds in which a methylphenoxy group attached at one end acts as a donor, the oxygen of the carbonyl group in the centre acts as an acceptor and methyl/dimethyl amino group attached to the other end acts as electron donor.

The nonlinear transmissions 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. The open aperture curve, closed aperture curve and pure nonlinear refraction curve of the samples are shown in Figs. 4–6, respectively. Fig. 3 shows the normalized transmission without an aperture at 532 nm. Here the curves are nearly symmetric with respect to focus ($z=0$), where it has a minimum transmission, showing an intensity dependent absorption effect. The shape of the open aperture curve suggests that the compound exhibits two photon absorption [13–16]. The model described in

[12] was used to determine the magnitude of the nonlinear absorption coefficient (β) and the third order susceptibility $\chi^{(3)}$ of the samples.

Further to determine the contribution of the solvent to the 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 normalized transmittance for the open aperture-scan is given by [12]

$$T(z) = \frac{\ln[1+q_0(z)]}{q_0(z)} \quad \text{for } |q_0(z)| < 1, \quad (1)$$

$$\text{where } q_0(z) = \frac{I_0 \beta_{\text{eff}} L_{\text{eff}}}{(1+z^2/z_0^2)}.$$

I_0 is the on-axis peak irradiance at the focus, L_{eff} is the effective thickness of the sample, β_{eff} is an effective value of the

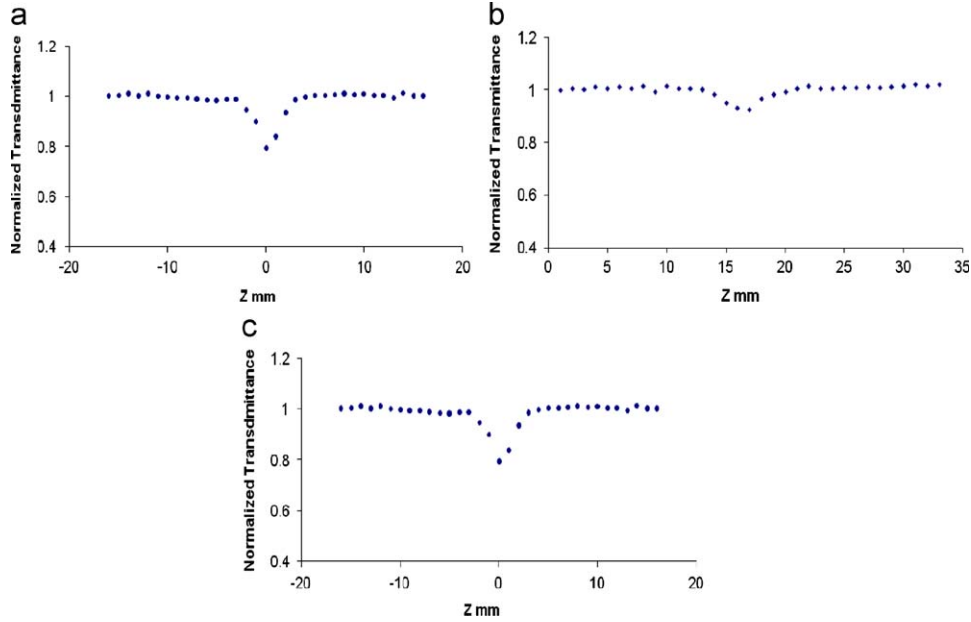


Fig. 4. Open aperture z-scan curves of compounds: (a) Compound-1, (b) compound-2 and (c) compound-3.

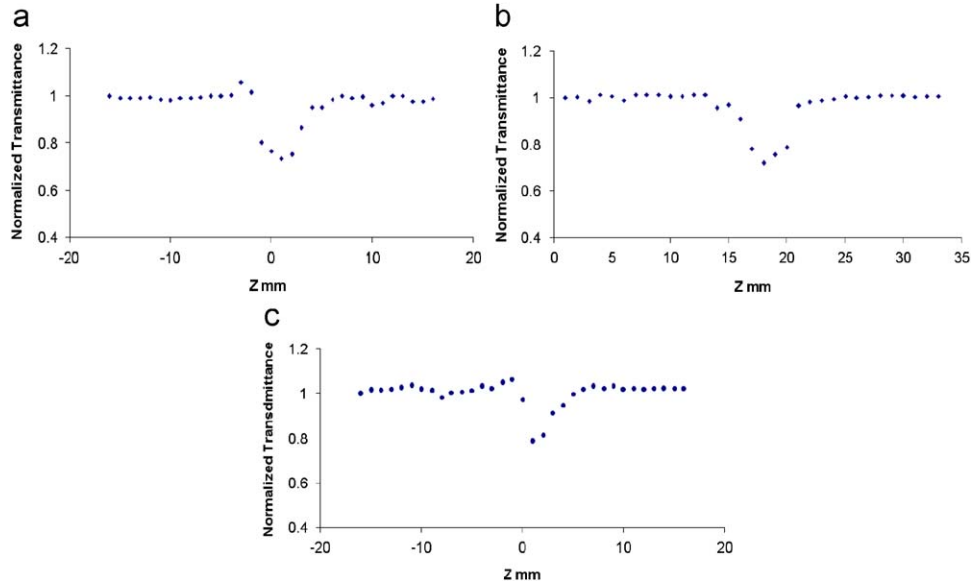


Fig. 5. Closed aperture z-scan curves of compounds: (a) Compound-1, (b) compound-2 and (c) compound-3.

two-photon absorption coefficient and z_0 is the Rayleigh length. The open aperture data of the compound was fitted with (1).

In order to extract the information on the 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 in front 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 (Fig. 5). To obtain a pure nonlinear refraction curve we used the division method described in [12]. The curve thus obtained by dividing closed aperture curve by open aperture curve is shown in Fig. 5. The peak and valley configuration of the 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 ($\Delta T_p - v$) in the pure NLR curve (Fig. 6) is used to calculate the nonlinear refractive index of the compounds using the relation

$$\gamma = \frac{\Delta\phi_0 \lambda}{2\pi L_{eff} I_0}, \tag{2}$$

where λ is the wavelength of the laser light and $\Delta\phi_0$ is the nonlinear phase shift given by the relation

$$\Delta\phi_0 = \frac{\Delta T_p - v}{0.406(1-S)^{0.25}} \quad \text{for } |\Delta\phi_0| \leq \pi, \tag{3}$$

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

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

$$\text{Re } \chi^{(3)} = 2n_0^2 \epsilon_0 c \gamma, \tag{4}$$

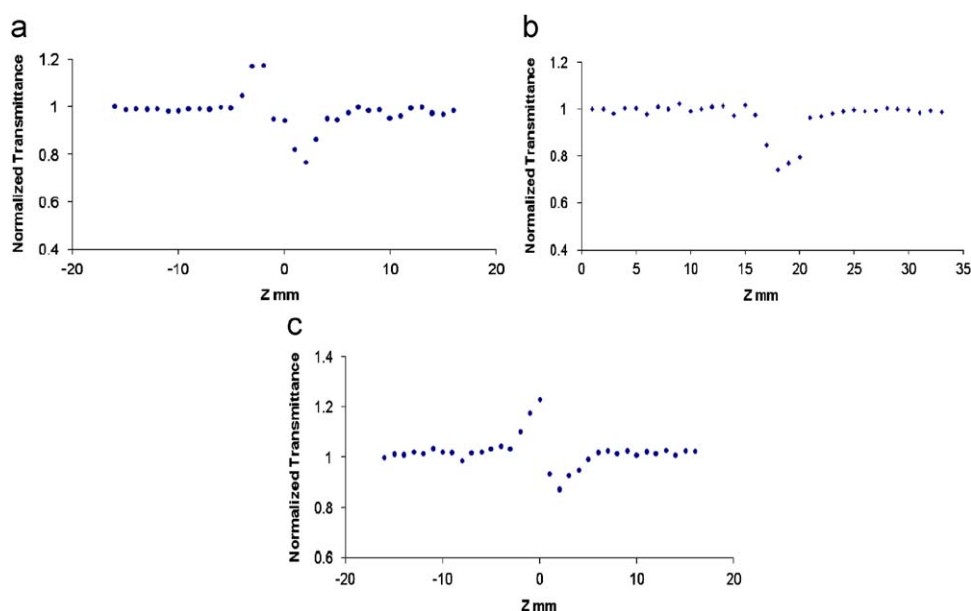


Fig. 6. Closed/open aperture z-scan curves of compounds: (a) Compound-1, (b) compound-2 and (c) compound-3.

Table 1

Experimentally determined values of the compounds.

Compounds	n_0	n_2 (esu)	β (cm/GW)	$\text{Re } \chi^{(3)}$ (esu)	$\text{Im } \chi^{(3)}$ (esu)
1	1.308	-0.79×10^{-11}	1.13	0.72×10^{-13}	0.14×10^{-13}
2	1.310	-0.53×10^{-11}	0.44	0.49×10^{-13}	0.05×10^{-13}
3	1.309	-0.69×10^{-11}	1.23	0.63×10^{-13}	0.15×10^{-13}

$$\text{Im } \chi^{(3)} = n_0^2 \epsilon_0 c \lambda \beta / 2\pi, \quad (5)$$

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

$$n_2 \text{ (esu)} = (cn_0/40\pi)\gamma \text{ (m}^2/\text{W)}. \quad (6)$$

The experimentally determined values of β , n_2 , $\text{Re } \chi^{(3)}$ and $\text{Im } \chi^{(3)}$ of the compounds are given in Table 1. These values are comparable with that of dibenzylideneacetone and its derivatives, reported by John Kiran et al. [17] and 4-methoxy chalcone derivatives, reported by Ravindra et al. [18]. These values are very much greater than that for the dmit organometallic complex BuCo [19] and cobalt-doped polyvinylpyrrolidone [20] solution.

The value of $\text{Re } \chi^{(3)}$ for compound-1 is 0.72×10^{-13} esu, which is larger than that for the other samples. The optical nonlinearity is closely related to the chemical structure of the compound and the nonlinear response can be explained based on the electron accepting/donating ability of the groups present in the molecule. The nonlinear response of the compound-1 is mainly due to the π -electron density in the molecule and the electron accepting ability of the nitro group in the molecule.

The compounds-2 and 3 are D–A–D type molecules. The nonlinear optical susceptibility was found to increase from compound-2 to compound-3. The observed increase in the nonlinear response may be due to the electron donating ability of the groups present in the molecule. The dimethyl amino group in compound-3 is a strong electron donor compared to methyl group in compound-2. Hence the charge transfer is more effective in compound-3 and shows a higher nonlinear response compared to compound-2. 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 π -electron delocalization and charge transfer contributes to the ultrafast optical response capability and large third order susceptibility.

Further compound-3 has more absorption at 532 nm compared to compounds-1 and 2. The nonlinear susceptibility of the molecules increased in the order, compounds $1 > 3 > 2$. The dependence of $\chi^{(3)}$ on donor/acceptor type substituents in these compounds clearly shows the nonlinearity is of electronic origin and the thermal effect does not play any dominant role in the third order nonlinear response of the compounds.

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 γ_h of a molecule in an isotropic medium is related to the third order susceptibility as follows:

$$\gamma_h = \chi^{(3)} / N_c L^4, \quad (7)$$

where N_c is the density of molecules (in the unit of number of molecules per cm^3) and L is the local field factor given by $L = (n^2 + 2)/3$; here n is the linear refractive index of the medium. 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 γ_h values obtained in the present investigation are comparable with the values reported for 4-methoxy chalcone

Table 2
Experimentally determined values of the compounds.

Compounds	$\Delta\phi_0$	γ_h (esu)	σ_2^1 (cm ⁴ s/photon)	ρ
1	1.42	0.51×10^{-32}	0.71×10^{-46}	0.19
2	0.96	0.34×10^{-32}	0.27×10^{-46}	0.11
3	1.25	0.44×10^{-32}	0.77×10^{-46}	0.24

derivatives, reported by Ravindra et al. [18] and with that of thiophene (hexamer) [21]. These values are found to be greater than that of thiophene (dimer, trimer, tetra and pentamers) [21].

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

$$\rho = \text{Im}\chi^{(3)} / \text{Re}\chi^{(3)}. \quad (8)$$

The observed values of the coupling factor ρ for the given molecules are around 1/3, indicating that the nonlinearity is electronic in origin.

It is known that the nonlinear absorption coefficient β depends on the number of absorptive centers in a unit volume. Assuming this number is N_0 in units of cm⁻³, then for a solution system, we have [22,23]:

$$\beta = \sigma_2, \quad N_0 = \sigma_2, \quad N_A d \times 10^{-3}. \quad (9)$$

Here N_0 is the molecular density of the sample, σ_2 is the molecular two photon absorption (TPA) coefficient of the same compound (in units of cm⁴/GW), d is the concentration of the compound in the solution (in units of mol/L), and N_A is the Avogadro number. For a known d , the value of σ_2 can be easily calculated.

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

$$\sigma_2^1 = \sigma_2 h\nu, \quad (10)$$

where σ_2^1 is in units of cm⁴ s and $h\nu$ is the energy (in joules) of an incident photon. 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} cm⁴ s/photon, which are comparable with that for chalcone derivatives in polymer host, reported by Seetharam Shettigar et al. [24].

The compounds-1 and 3 show better optical limiting at 532 nm wavelength (Fig. 7), compared to compound-2. They exhibit strong two photon absorption at that wavelength. For a concentration of 1×10^{-2} mole/l, the output energy increases linearly with the incident energy upto input energies of 325 $\mu\text{J}/\text{pulse}$. But for energies more than this, the output energy is almost constant assuming the value of 208 $\mu\text{J}/\text{pulse}$.

The nonlinear absorption increases with the increase in concentration. For compound-1, when the concentration is increased to 2×10^{-2} mole/l, the output energy increases linearly with the increase in input energy, till 150 $\mu\text{J}/\text{pulse}$. With further increase in the input energy, the output energy gets stabilized to nearly a constant value of 120 $\mu\text{J}/\text{pulse}$. It is seen that the power limiting threshold decreases with increasing concentration. In the case of higher concentration (4×10^{-2} mole/l), the output energy increases linearly with the incident energy and for energies more than 150 $\mu\text{J}/\text{pulse}$, the output energy is almost clamped around 100 $\mu\text{J}/\text{pulse}$ (Fig. 8).

For compound-3, when the concentration is increased to 2×10^{-2} mole/l, the output energy increases linearly with the increase in input energy, till 225 $\mu\text{J}/\text{pulse}$. With further increase in the input energy, the output energy gets stabilized to nearly a constant value of 180 $\mu\text{J}/\text{pulse}$. It is seen that the power limiting threshold decreases with increasing concentration. In the case of higher concentration (4×10^{-2} mole/l), the output energy increases linearly with the incident energy and for energies more

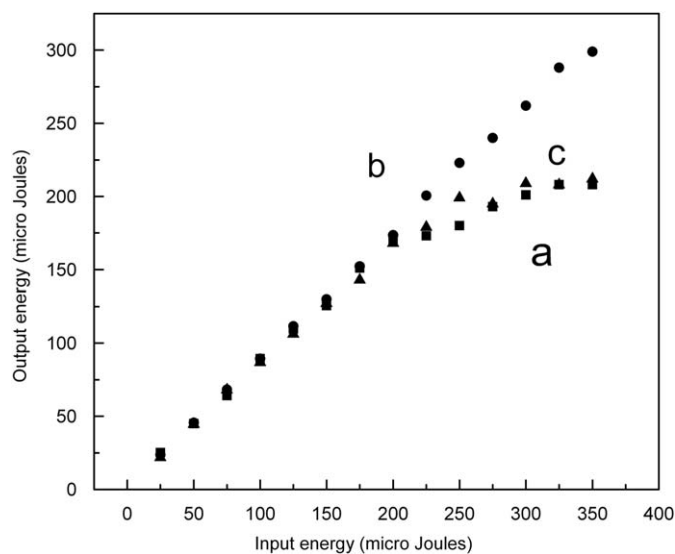


Fig. 7. Optical limiting of compounds-1, 2 and 3.

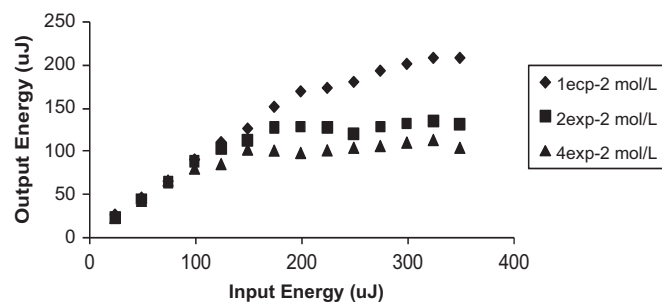


Fig. 8. Optical limiting of compound-1 for different concentrations.

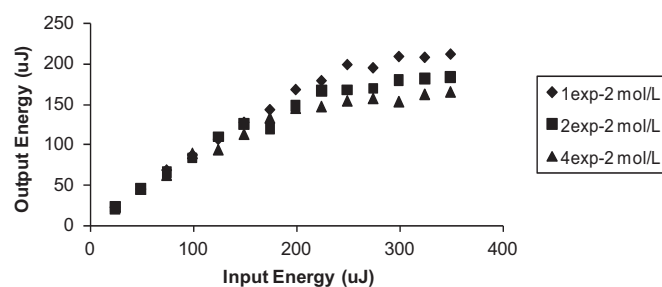


Fig. 9. Optical limiting of compound-3 for different concentrations.

than 200 $\mu\text{J}/\text{pulse}$, the output energy is almost clamped around 160 $\mu\text{J}/\text{pulse}$ (Fig. 9). This effect is due to the two photon absorption [25].

The basic requirements for optical limiting applications, i.e. large nonlinear refraction and positive nonlinear absorption were observed in the reported hydrazones. The large nonlinearities of the reported compounds are due to the delocalized electronic states [26]. Our studies suggest that compounds-1 and 3 are potential candidates for the optical device applications such as optical limiters and optical switches.

4. Conclusion

Three hydrazone compounds were synthesized and their third order nonlinear optical properties were investigated using a single

beam z-scan technique with nanosecond laser pulses at 532 nm. Open aperture data of other compounds demonstrate the occurrence of two photon absorption at this wavelength. The nonlinear refractive index, nonlinear absorption coefficient and magnitude of effective third order susceptibility have been estimated. The values obtained are comparable with the values obtained for 4-methoxy chalcone derivatives and dibenzylideneacetone derivatives. All the compounds show optical limiting behaviour at 532 nm. The compound-3 exhibits the best optical limiting property at 532 nm among the three compounds studied. These compounds may be used for the optical device applications such as optical limiters and optical switches. Thus it is possible to tailor materials with large nonlinear optical property through structure modification in hydrazones by the introduction of donor/acceptor groups to the bridge.

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