

Synthesis, characterization and studies on nonlinear optical parameters of 4-amino-5-(4-nitrophenyl)-1, 2, 4-triazole-3-thione

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Abstract In this paper, we report the synthesis, characterization and third order nonlinear optical properties of a new organic NLO material of 4-amino-5-(4-nitrophenyl)-1, 2, 4-triazole-3-thione (ANIT). The material was characterized by UV–vis and FTIR studies. The third order nonlinear optical properties have been investigated in dimethyl formamide (DMF) solution at 532 nm by using the Z-scan technique with pulses of nanoseconds duration. Open aperture data demonstrates the presence of two photon absorption at this wavelength. The nonlinear absorption coefficient β , the nonlinear refractive index n_2 , the magnitude of effective third order susceptibility $\chi^{(3)}$ and the second order hyperpolarizability γ_h have been estimated as 2.99 cm/GW, -2.53×10^{-11} esu, 2.72×10^{-13} esu and 0.281×10^{-31} esu respectively. The values obtained are comparable with the values obtained for 4-methoxy chalcone derivatives and dibenzylideneacetone derivatives. The value of coupling factor have been estimated to be 0.17, indicating that the nonlinearity is electronic in origin. The compound exhibits good optical limiting at 532 nm with the limiting threshold of 80 μ J/pulse. The comparatively high value

obtained indicates that this material may be used in optical device applications like optical limiters and optical switches.

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

Introduction

Third-order nonlinear optical (NLO) materials have attracted considerable attention due to their potential applications including optical switching, optical limiting, signal processing, ultra fast optical communications etc. [1, 2]. Various kinds of chemical materials, such as inorganic oxides, semiconductors, conjugated polymers and organic and organometallic materials have been found to exhibit good third-order NLO properties. Organic materials, in particular, with the structure of extensively delocalized pi-electrons have received significant attention recently due to their large NLO susceptibilities, architectural flexibility and ease of fabrication [3–8].

Nonlinear optical (NLO) materials which possess a high NLO chromophore density so as to display large optical nonlinearity, low optical losses and ultra fast response time can be used in photonic devices. A combination of these features in a material is very important for third order NLO applications.

Organic materials have been extensively studied due to their nonlinear optical coefficients being larger than those of inorganic materials. The NLO effects in the organic molecules originate from a strong donor-acceptor intermolecular interaction, delocalized pi-electron system and also due to the ability to crystallize in non-centro symmetric manner. Nonlinear optical materials with large intensity dependent refractive index and absorption coefficient are very useful for optical device applications. These param-

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ters determine whether an intense laser beam will undergo self-focusing or self defocusing as it propagates in the material medium [9].

Recently, organic materials have drawn significant attention as optical limiters for sensor protection from laser terror in homeland or agile laser threats on the battlefield. Optical limiters are devices that transmit light at low input fluences or intensities and at high inputs, the transmitted light intensity gets damped at a low value. The optical limiting property occurs mostly due to absorptive nonlinearity which is proportional to the imaginary part of third order optical susceptibility. In general, optical limiting property is facilitated by the presence of strong nonlinear absorption whereas the presence of nonlinear refraction is good for the switching property of organic molecules.

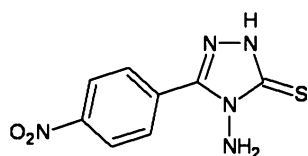
In this paper, we report for the first time our experimental investigation on the nonlinear optical properties of 4-amino-5-(4-nitrophenyl)-1,2,4-triazole-3-thione (ANIT) in the solution form in dimethyl formamide (DMF) solvent. The nonlinear refractive index n_2 , the nonlinear absorption coefficient β and the magnitude of third order nonlinear optical susceptibility $\chi^{(3)}$ were estimated, with the single beam Z-scan technique at 532 nm.

Materials and methods

The title compound was obtained from p-nitro benzoic acid, which on esterification with ethanol in the presence of concentrated sulphuric acid as a catalyst yields the corresponding ester. This ester on hydrazinolysis with hydrazine hydrate in ethanol gives p-nitro benzoyl hydrazine. The hydrazide thus obtained was converted to its potassium dithiocarbazinate by stirring with carbon disulphide in alcoholic KOH. Obtained potassium dithiocarbazinate and hydrazine hydrate were gently heated in presence of water. Heating was continued until the evolution of hydrogen sulfide ceased. The reaction mixture was cooled to room temperature and diluted with water. It is then acidified with dilute HCl. The solid mass separated was collected by filtration, washed with water and dried to get the final compound 4-amino-5-(4-nitrophenyl)-1,2,4-triazole-3-thione. Recrystallisation was done from ethanol to get pure crystals. The structure of the compound is given in Fig. 1.

The UV-visible spectrum was recorded using a SHIMADZU UV-VIS-NIR scanning spectrophotometer, model

Fig. 1 Structure of ANIT



3101 PC (Fig. 2). The FTIR spectrum of the grown crystal was recorded in the KBr phase within the frequency region 400–4,000 cm^{-1} , using SHIMADZU 8400S FTIR spectrometer (Fig. 3).

The single beam Z-scan technique is an increasingly popular method for the measurement of optical nonlinearities of materials, not only because it has the advantages of simplicity and high sensitivity, but also it can simultaneously measure the magnitude and sign of the nonlinear refractive index and the nonlinear absorption coefficient of the sample [10]. It is used to measure the nonlinear susceptibility of the sample. 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 enough to induce nonlinearity in the sample, it either converges the beam (self focusing) or diverges (self defocusing), depending on the nature of 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 spot size variation at the plane of a finite aperture detector combination (closed aperture) because the sample itself acts as a thin lens with varying focal length as it moves through the focal plane.

The third order nonlinear optical susceptibility of the sample was investigated by the Z-scan technique. 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. The solution of ANIT in DMF was prepared with a concentration of 5×10^{-3} mol/L. The Gaussian laser beam was focused into the sample solution contained in a 1 mm quartz cuvette, using a lens of focal length 25 cm. The

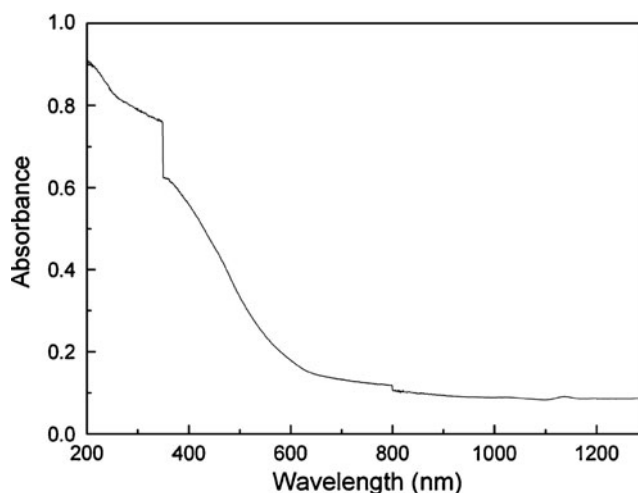
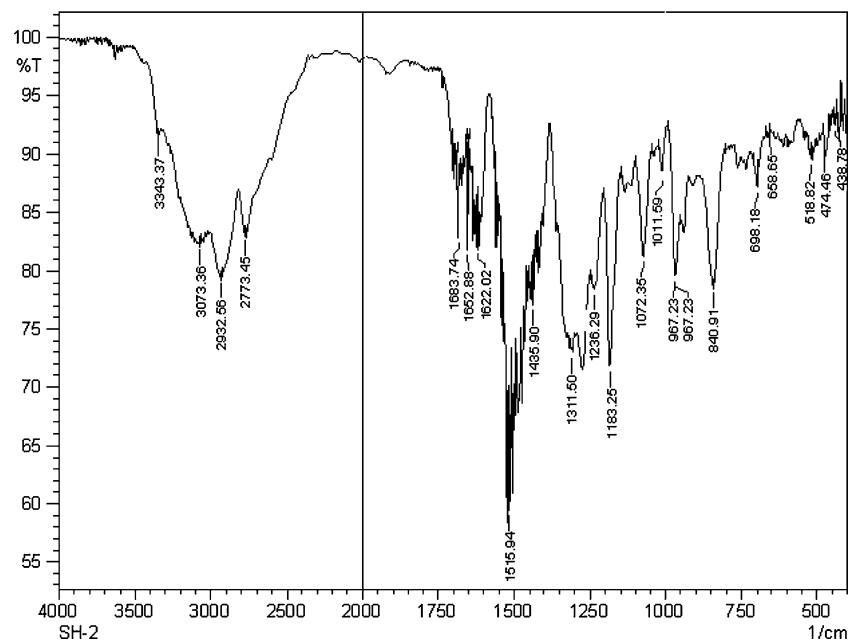


Fig. 2 Linear absorption spectrum of ANIT

Fig. 3 FTIR spectrum of ANIT

resulting beam waist radius at the focus was calculated using the formula, $\omega_0 = 1.22f \lambda/d$, 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 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. The experiment was carried out at room temperature. In order to avoid the cumulative thermal effect, the data were collected in a single-shot mode [11].

Theory

The nonlinear transmission of compounds with and without aperture was measured in the far field as the sample was moved through the focal point. This helps us to separate the nonlinear refraction from the nonlinear absorption. The open aperture curve, closed aperture curve and pure nonlinear refraction curve of samples are shown in the Figs. 4, 5, and 6 respectively. Figure 4 shows the normalized transmission without an aperture at 532 nm. Here the transmission is

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 [12–15]. The model described in [10] was used to determine the magnitude of nonlinear absorption coefficient β of the samples.

Further to determine the contribution of the solvent to n_2 , we conducted Z-scan experiment on pure DMF and found that neither nonlinear refraction nor nonlinear absorption was observed at the input energy used. Hence any contribution from the solvent to the nonlinearity of the sample is negligible.

The normalized transmittance for the open aperture-scan is given by [10]

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

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

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

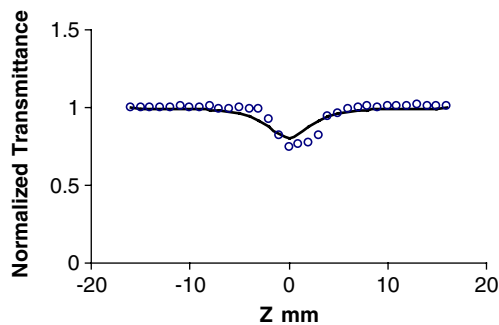


Fig. 4 Open aperture Z-scan curve of ANIT

with an aperture placed at the far field. In almost all materials, the nonlinear refraction (NLR) is accompanied by the nonlinear absorption (NLA); thus, in the case of negative refractive nonlinearity, the transmittance curve for the closed aperture Z-scan has a suppressed peak and an enhanced valley (Fig. 5). To obtain a pure nonlinear refraction curve, we used the division method described in [10]. The curve thus obtained by dividing closed aperture curve by open aperture curve is shown in Fig. 6. The peak and valley configuration of the curve clearly indicates the negative sign of the 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 (T_{p-v}) transmittance in the pure NLR curve is used to calculate the nonlinear refractive index of the compounds using the relation

$$\gamma = \frac{\Delta\phi_0\lambda}{2\pi L_{\text{eff}}I_0}, \quad (2)$$

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

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

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

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

$$\text{Re}\chi^{(3)} = 2n_0^2\varepsilon_0c\gamma \quad (4)$$

$$\text{Im}\chi^{(3)} = n_0^2\varepsilon_0c\lambda\beta/2\pi, \quad (5)$$

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

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

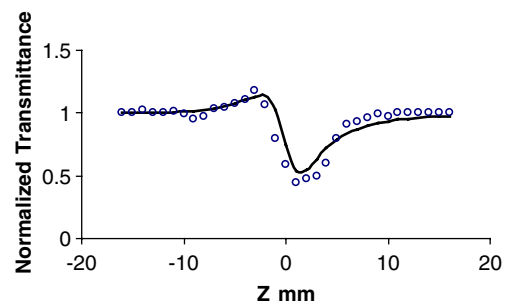


Fig. 5 Closed aperture Z-scan curve of ANIT

The second order hyperpolarizability γ_h of a molecule in an isotropic medium is related to the macroscopic third order susceptibility as follows [3]:

$$\gamma_h = \chi^{(3)}/N_cL \quad (7)$$

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 $L = [(n^2 + 2)/3]^4$, where n is the linear refractive index of the medium.

The coupling factor ρ is the ratio of imaginary part to real part of third order nonlinear susceptibility. ie;

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

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 [16, 17],

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

Here N_0 is the molecular density of the sample, σ_2 is the molecular TPA coefficient of the same compound (in units of cm^4/GW), d is the concentration of TPA 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

$$\sigma_2^{-1} = \sigma_2 h\nu \quad (10)$$

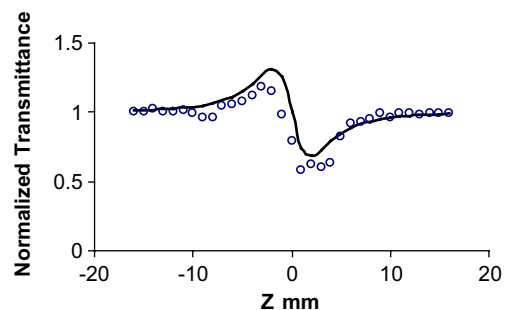


Fig. 6 The curve obtained by dividing the closed aperture data by the open aperture data of ANIT

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

Results and discussion

Spectroscopic characterization

The UV visible spectrum was recorded using a SHIMADZU UV–VIS–NIR scanning spectrophotometer, model 3101 PC. There is negligible absorption of light at 532 nm (Fig. 2). The FTIR spectrum of the grown crystal was recorded in the KBr phase within the frequency region 400–4,000 cm^{-1} , using SHIMADZU 8400S FTIR spectrometer. IR vibrational spectrum is presented in Fig. 3. The peak at 3,343 cm^{-1} corresponds to the NH stretching vibration. The C = N vibration appears at 3,073 cm^{-1} . Between 3,000 and 2,800 cm^{-1} , the band of 2,932 cm^{-1} is associated with C–H stretching vibrational mode. The band at 1,683 cm^{-1} corresponds to C = O vibration while C = C vibration appears at 1,652 cm^{-1} . The very strong peak observed at 1,516 cm^{-1} is attributed to asymmetric stretching vibration of N = O. The symmetric vibration of N = O appears at 1,311 cm^{-1} . The peak at 1,183 cm^{-1} corresponds to the C = S vibration. The deforming C–H is seen at 967 cm^{-1} and 840 cm^{-1} is assigned to C–C stretching.

Third-order nonlinear optical properties

The experimentally determined values of β , n_2 , $\text{Re } \chi^{(3)}$ and $\text{Im } \chi^{(3)}$ are 2.99 cm^2/GW , -2.53×10^{-11} esu, 2.72×10^{-13} esu and 0.46×10^{-13} esu respectively. These values are comparable with that of dibenzylideneacetone and its derivatives, reported by John Kiran et al. [18] and 4-methoxy chalcone derivatives, reported by Ravindra et al. [19]. These values are very much greater than that for the dmit organometallic complex BuCo [20] and Cobalt-doped Polyvinylpyrrolidone solution [21].

The microscopic second order hyperpolarizability of the compound is calculated to be 0.281×10^{-31} esu. This value can be compared with the values of organic molecules and polymers reported in the literature. The γ_h values obtained in the present investigation is better than the values reported for 4-methoxy chalcone derivatives, reported by Ravindra et al. [19] and greater than that of thiophene (dimer, trimer, tetra and pentamers) [22]. Also found that it is comparable with the values reported for copolymers by John Kiran et al. [23], chalcone derivatives in polymer host, reported by Seetharam Shettigar et al. [24], thiophene (hexamer) [22] and that of substituted benzohydrazides [25].

The observed value of the coupling factor ρ for the given molecule is 0.17 which is less than 1/3, indicates that the nonlinearity is electronic in origin. It is found that the

effective TPA cross-section of the compound ANIT is 3.39×10^{-46} $\text{cm}^4\text{s}/\text{photon}$. It is found to be greater than that for chalcone derivatives in polymer host, reported by Seetharam Shettigar et al. [24].

The title compound shows good optical limiting at 532 nm (Fig. 7). It exhibits strong two photon absorption at that wavelength. The nonlinear absorption increases with the increase in concentration. For a concentration of 5×10^{-3} mole/litre, the output energy increases linearly with the increase in input energy, till 250 $\mu\text{J}/\text{pulse}$. With further increase in the input energy, the output energy gets stabilized to nearly a constant value of 150 $\mu\text{J}/\text{pulse}$. It is seen that the power limiting threshold decreases with increasing concentration. In the case of higher concentration (15×10^{-3} mole/litre), the output energy increases linearly with the incident energy up to input energies of 250 $\mu\text{J}/\text{pulse}$. But for energies more than this, the output energy is almost constant assuming the value of 80 $\mu\text{J}/\text{pulse}$. This effect is due to the two photon absorption [26]. Since the title compound possess interesting optical limiting properties, it can be used in many application areas such as optical limiters and optical switches.

The basic requirements for optical limiting applications, like large nonlinear refraction and positive nonlinear absorption are observed in the title compound ANIT. It is confirmed by the presence of optical limiting. The large nonlinearities of the title compound are due to the delocalized electronic states [27]. The optical nonlinearities are closely related to the chemical structure of the compound. The compound exists in thio-enol tautomeric forms.

The title compound is a donor–acceptor type of conjugated system in which nitro phenyl group acts as an acceptor and the pi electron rich heterocyclic ring containing NH_2 and sulphur, as the donor. The pi electron

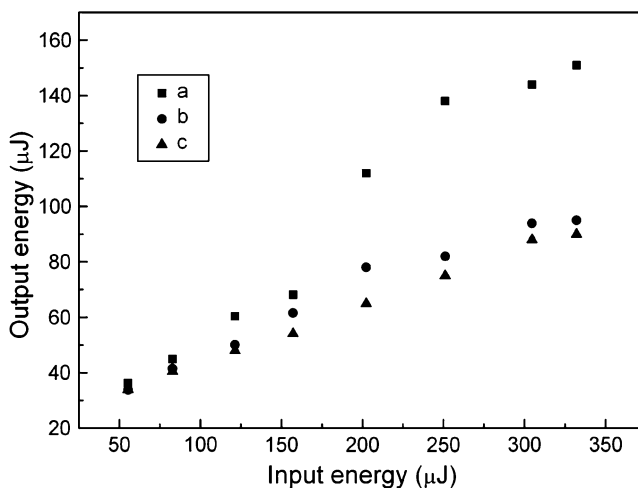


Fig. 7 Optical limiting of laser pulses in the compound ANIT for different concentrations **a** 0.5×10^{-2} mole/litre, **b** 1×10^{-2} mole/litre, **c** 1.5×10^{-2} mole/litre

delocalization and charge transfer contributes to the ultra fast optical response capability and large third order susceptibility. Delocalization also enhances the second order hyperpolarizability of the molecule.

Conclusion

A new organic compound with third order nonlinear optical properties has been synthesized and characterized by spectroscopic analysis. The third order nonlinear optical properties of the compound in DMF solution with the concentration of 5×10^{-3} mol/L at 532 nm were investigated by using the Z-scan technique with pulses of eight nanoseconds duration. Open aperture data demonstrates the presence 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 and better than the dmit-organometallic complex BuCo and Cobalt-doped Polyvinylpyrrolidone solution. The observed value of the coupling factor ρ for the given molecule (0.17) indicates the electronic origin of nonlinearity. The compound exhibits good optical limiting at 532 nm with the limiting threshold of 80 $\mu\text{J/pulse}$. The comparatively high value obtained indicates that this material is a potential candidate for the optical device applications such as optical limiters and optical switches.

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