Characterization of the nonlinear optical properties of the new 2-amino-4,6-difenilnicotinonitrilo by UV-Vis spectroscopy absorption and Z-Scan

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Abstract. The study of the nonlinear optical properties of new organic molecules in solution was performed. Z-Scan technique was used to investigate the nonlinear optical properties of 2-amino-4,6-diphenylnicotinonitrile depending on the solution concentration and the laser power; This compound was diluted in ethyl acetate at fixed concentration of 0.024M. Through this technique, nonlinear parameters such as the nonlinear refractive index ($\eta_2$), the nonlinear absorption coefficient ($\beta$) and the third-order electric susceptibility ($\chi^3$) were determined. For these measurements, a laser Nd: YAG emitting at 532nm, a lens 10 cm focus, an iris of 1mm and a cell with a thickness of 1mm were used. The study was performed with laser powers of 55mW, 100mW, 145mW and 195mW; All measurements were made by transmission in closed and open configurations. Finally the sample was characterized by absorption spectroscopy UV-Vis. This study allows us to relate the molecular design with the optical properties.

1. Introduction
The aminodiphenylnicotinonitriles are compounds very interesting because they possess a pyridine structure, which is known to have biological activity, they also have an amino group at position 2 and a cyano group in position 3 according to the numeration of pyridine ring IUPAC; allowing cyclocondensation reactions, nucleophilic addition reactions bidentate ligands and therefore are synthesized by conventional and no conventional methods [1].

This compound has a conjugated system or delocalization of the $\pi$ orbital, which makes it possible participant in charge of transfer processes. Furthermore, they can be synthesized incorporating appropriate substituents on the aromatic rings so that each ring may confer characteristics like charge donor or acceptor [2-4]. These charge transfer characteristics and polarizability could make these materials suitable as raw materials for optoelectronic applications [5].

Organic materials with nonlinear optical responses are very interesting in this subject because their time response is fast; they are inexpensive, easy to process and exhibit thermal and chemical stability, among other advantages. The structural requirement to be satisfied by organic materials that can show nonlinear optical phenomena is the presence of a lattice of electron $\pi$-conjugated delocalized, which confer a high polarizability and rapid charge redistribution when the conjugated molecule interacts with intense and rapidly variable electromagnetic fields as the ones obtains with laser. The large and ultrafast nonlinearity of these materials can be used in different applications such as optical switches, optical modulators, optical signal processing and as optical limiters [6].

Z-Scan technique [7] is used to monitor the transmittance of the sample according to their position $Z$ on the position of the focal plane of the main lens [8]. Scan range required depends on the beam
parameters and the sample thickness. The nonlinear optical effects are due to the nonlinear properties of the sample such as changes in the refractive index and absorption coefficient that is taken in the incidence of a beam of high intensity light such as a laser [9,10].

Nowadays, there are not any reports of an optical study done on 2-amino-4,6-diphenylnicotinenitriles. Therefore a detailed analysis of the nonlinear optical properties is performed for a better understanding of the system $\alpha, \beta$-unsaturated.

2. Experimental technique

2.1. Synthesis of 2-amino-4,6-diphenylnicotinenitrile

The synthesis of this compound occurs by heating till melting temperature by mixing one mmol (198.04mg) 2-benzylidenemalononitrile, previously synthesized from piperonal with malononitrile through a Knoevena gel condensation; with acetophenone (0.116mL) and ammonium acetate (770mg) through pyridine syntheses of Hantzsch. The mixture was melted in a 10mL balloon at 200°C for 30 minutes. During reaction, the mixture was controlled by thin layer chromatography (TLC), after that ethanol was added and heated for 10 minutes. After reaction, the mixture is allowed to stand until it reaches room temperature. The resulting precipitate was filtered, washed with cold ethanol, dried and recrystallized. Synthesis reaction is shown in Figure 1.

![Figure 1. Synthesis of 2-amino-4,6-diphenylnicotinenitrile.](image)

2.2. Characterization of the sample by UV-Vis spectroscopy

The UV-Vis spectrum of the sample was recorded in the wavelength range of 200 to 800nm using a UV-Vis spectrophotometer EVOLUTION60S ThermoScientific, sample preparation was made at a concentration of 20mg/L. The spectrum is shown in Figure 2. It is observed in the spectrum that 2-amino-4,6-diphenylnicotinenitrile absorbs light at a wavelength of 355nm; where it is possible to use a laser emitting at 532nm, since no absorption is observed at this wavelength presenting high transmittance, which is suitable for experiments with Z-Scan.

![Figure 2. UV-Vis spectrum of 2-amino-4,6-diphenylnicotinenitrile.](image)
3. Results and Discussion

Through the Z-Scan technique were carried out measurements using a laser Nd: YAG doubled in frequency emitting at 532nm and focused by a lens 10cm, a radius belt 27 microns at the focal point, the radius of the beam waist of the laser is 1.25mm, as shown in Figure 3; the sample was placed in a glass cell with thickness of 1mm. 2-amino4,6-diphenylenilnicotinenitrile under study was diluted in ethyl acetate at a fixed concentration of 0.024 M, measurements were performed at different laser power: 55mW, 100mW, 145mW and 195mW.

Figure 3. Experimental set of the Z-Scan technique.

The Z-Scan technique is a method used frequently to determine the nonlinear refractive index ($\eta_2$), the nonlinear absorption coefficient ($\beta$) and the third-order electric susceptibility ($\chi^3$) in certain materials.

As proposed by Sheik-Bahés theoretical mathematical model, the nonlinear refractive index ($\eta_2$) was calculated by:

$$\Delta T_{pv} = 0.406 (1 - S)^{0.25} |\Delta \Phi|$$

(1)

Where he $\Delta \Phi$ is the phase shift in the focus axis and is expressed by $|\Delta \Phi| = k n_1 I_0 L_{eff}$ and $I_0 = P/\pi \omega_0^2$ is the intensity of the laser.

Solving $n_2$ in Equation 1, and replacing it in the expression above, we obtain:

$$n_2 = \frac{\Delta T_{pv} \omega_0^2 \lambda}{1.624 (1 - S)^{0.25} P L_{eff}}$$

(2)

Using the Rayleigh parameter definition is obtained:

$$n_2 = \frac{\Delta T_{pv} \Delta Z_{pv} (\lambda)^2}{2.7608 \pi P L_{eff}}$$

(3)

Equation 3 is used to obtain $n_2$ where $\Delta T_{pv}$ can be defined as the difference between the peak and the valley of the normalized transmittance ($T_p - T_v$), $\Delta Z_{pv}$ is the difference of displacement in the Z path, $\lambda$ is the length of laser wave, $P$ is the power emitted and $L_{eff}$ laser is the cell thickness.

In Figure 4, variations in the nonlinear optical properties of the material in function of the laser power are observed. For displacement between 60mm and 100mm the emergence of an effect of thermal origin primarily to high power, due to local heating of the sample at the point where laser is located. On power of 55mW, thermal and nonlinear effects are less intense.

To obtain $\beta$, we proceed to remove the iris in assembling to the Z-Scan. From this normalized transmittance curve in open configuration (Figure 5), we were able to calculate $\beta$. 


\[ \beta = \frac{2^{(2(\Delta T_{vp}))^{1/2}}}{I_0 L_{\text{eff}}} \] (4)

Where \( I_0 \) is the intensity of laser beam, \( \Delta T_{vp} \) is the difference between valley and peak of the normalized transmittance curve for the open cell configuration, and \( L_{\text{eff}} \) is cell thickness.

A comparison Z-Scan scanning in open cell configuration is shown in Figure 5, for different laser powers. The emergence of the thermal effect on the 2-amino-4,6-diphenylnicotinenitrile for a laser power of 55mW is smaller, but has less nonlinearity, opposite occurs in the curve of 195mW of laser power, where the thermal effect is greater compared to the other laser power, but this shows a better nonlinearity. The thermal effect increases when increasing laser power. Furthermore it is observed that close to 195mW power curves suffer a widening indicating that the thermal effect produced by the laser focused on the sample begins to be significant, this effect observed in the curve Z-Scan.

For determining the third-order electric susceptibility (\( \chi^3 \)) the following equation is used:
\[ \text{Re} \chi^3(\text{esu}) = \left( \frac{10^{-4} \epsilon_0 c^2 n_0^2}{\pi} \right) n_2 \] (5)

Where \( \epsilon_0 \) is the electric permittivity, \( c \) is light speed, \( n_0 \) is the refractive index of material obtained from Snell's law and \( n_2 \) is the nonlinear refractive index.

Figure 6 and 7 shows that the nonlinear refractive index and nonlinear absorption coefficient, depending on the potency show linear behaviour.

**Figure 6.** Nonlinear refractive index variation depending on the laser power according to Table 1 for 2-amino-4,6-diphenylnicotinenitrile.

**Figure 7.** Variation of nonlinear absorption Coefficient based on the laser power according to Table 1, for 2-amino-4,6-diphenylnicotinenitrile.
Table 1. Optically nonlinear parameters calculated for the 2-amino-4,6-diphenylnicotinenitrile at a concentration of [0.024M] in different power.

| Power (mW) | Refractive index nonlinear | Absorption coefficient nonlinear | Electric susceptibility of third order |
|------------|---------------------------|----------------------------------|----------------------------------------|
|            | ΔTpv (u.a) | ΔZpv (cm) | n₂ (cm²/W) | ΔTvp (u.a) | I₀ (W/cm²) | β (cm/W) | n₀ | Re (χ₃) (esu) |
| 55         | 0.0248     | 1.4788    | 21.7589×10⁻¹⁰ | 5.3×10⁻¹ | 2402.7959 | 8.5697×10⁴ | 6.3272×10⁻¹² |
| 100        | 0.0318     | 1.7826    | 18.4977×10⁻¹⁰ | 13.7×10⁻¹ | 4368.7199 | 7.5779×10⁴ | 5.3789×10⁻¹² |
| 145        | 0.0415     | 1.6251    | 15.1774×10⁻¹⁰ | 22.0×10⁻¹ | 6334.6439 | 6.6227×10⁴ | 4.4134×10⁻¹² |
| 195        | 0.0533     | 1.2865    | 11.4746×10⁻¹⁰ | 27.8×10⁻¹ | 8519.0039 | 5.5357×10⁴ | 3.3367×10⁻¹² |

4. Conclusion

From normalized transmittance curves obtained from technical Z-Scan, it were achieved characterize the various parameters of non-linear optics of 2-amino-4,6-diphenylnicotinenitrile, as shown in Table 1, where it was observed that each parameter decreases as was increased laser power.

Experimental results of these parameters were obtain by first time, in which the study was conducted at different laser power, resulting in a variation on properties of the compound was obtained first, allowing accurate value determined for each power.

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