Synthesis, spectroscopic characterization and determination of the nonlinear optical properties of 2-(4-chlorobenzylidene) malononitrile using a computational method and Z-scan technique

A Rodelo\textsuperscript{1}, A Pérez\textsuperscript{1}, and F J Racedo\textsuperscript{2}

\textsuperscript{1} Grupo de Compuestos Heterocíclicos, Universidad del Atlántico, Puerto Colombia, Colombia
\textsuperscript{2} Grupo de Espectroscopía Óptica de Emisión y Laser (GEOEL), Universidad del Atlántico, Puerto Colombia, Colombia

E-mail: fran@mail.uniatlantico.edu.co

Abstract. A synthesis and theoretical study was carried out on UV-vis spectra of 2-(4-chlorobenzylidene) malononitrile. The structure, the geometry optimization, and the properties of non-linear optics were also investigated using the theory level M062X/6311++G (d, p). The Z-scan technique was used to establish the optical properties of 4ClD2MM as a function of the laser emission power; said compound was diluted in tetrahydrofuran to a fixed concentration of 0.1 M. By means of the same technique it was possible to establish non-linear parameters such as the non-linear refractive index, the non-linear absorption coefficient and the electronic third-order susceptibility. For these measurements, a Nd: YAG CW laser was used emitting at 532 nm, as well as a focus of a 10 cm lens, a 1 mm iris and a cell with a length of 1 mm.

1. Introduction
Materials with high nonlinear optical response (NLO) are of great technological interest due to their potential applications in data storage, signal processing and telecommunications technologies [1]. In particular, materials based on organic molecules such as active NLO centers are especially attractive due to their easy handling and short response time. The theoretical investigations have been of great help in the achievement of these results; they gave the first clues about the possible high NLO responses of organic molecules with a conjugated extended system [2–4]. In addition, they have been used in recent years as an a priori tool to calculate the NLO properties of organic molecules together with the other experimental methods [5–7]. The computational methods are beneficial since we obtain the previous understanding of the structure of influence in relation to the properties and the factors that govern the efficiency of NLO properties, such as the substituents contained in the system. In this case, the compound under consideration is an arylidene derivative whose system is of the "push-pull" type, that is, a compound with an electron donor fragment (D) and another electron acceptor (A) covalently linked through a spacer, which must have a delocalized electron system as show in Figure 1.
2. Theory

2.1. Chemical-quantum calculations

The hyperpolarizability ($\beta$), which is a measure of the nonlinear optical activity of a molecular system, is associated with the intermolecular charge transfer activity that results from the movement of the electron cloud through the conjugated structure $\pi$, which is moves in the direction of the electron donor group to the electron acceptor group [8]. Molecules with a large dipole moment and a means to change the density will have large hyperpolarizabilities, in general, it can be said that the property depends on the strength of the donor and acceptor groups, as well as the length and load delocalization in the system that unites them. On the other hand, in systems with substituted aromatic rings the planar affects and influences the size of the $\pi$ electron system and the mobility of electrons. The nonlinear optical properties of the compound under study were calculated, such as dipole moment ($\mu$), polarizability ($\alpha$) and hyperpolarizability ($\beta$) which use the components $x$, $y$, $z$; the latter being the one that determines the optical non-linearity of the molecules. Equation (1) to Equation (4) [9] were used to calculate these parameters. The Equation (1) and Equation (2) show the components used to determine the dipole moment and the mean value of the polarizability respectively.

The total static dipole moment ($\mu$), using the components $x$, $y$ and $z$ are defined as:

$$\mu_{tot} = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}$$ (1)

The average polarizability $\alpha_{total}$ which is defined as:

$$\alpha_{tot} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$ (2)

Equation (3) shows the components used to determine hyperpolarizability. In the first-order hyperpolarizability, the components of $\beta$ can also be observed as coefficients in the expansion of a Taylor series of energy in the external electric field when the external electric field is weak and homogeneous, this expansion is shown in Equation (4).

$$\beta_{tot} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$$ (3)

so:

$$\beta_{tot} = \left[ (\beta_{xxx} + \beta_{xxy} + \beta_{xxz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxz})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{\frac{1}{2}}$$ (4)
2.2. Z-scan technique

The Z-scan technique provides information on the value and sign of the non-linear refractive coefficient $\eta_2$, as well as the value and sign of the non-linear absorption coefficient $\beta$ [10]. The higher second-order susceptibilities are called non-linear susceptibilities linear $\chi^3$, are the cubic behavior of the susceptibility and originates non-linear phenomena of the third order. Non-linear processes of the third order are generated when the electric field incident in the non-linear medium is composed, in general, of three terms that oscillate at the frequencies $\omega_1, \omega_2$ and $\omega_3$. And the polarization of the third order of the medium is proportional to the third order of the incident field [11].

3. Metodology

3.1. Experimental: Synthesis of the compound and characterization by Z-scan

The synthesis of the molecules occurs through the Knoevenagel condensation [12]. Equimolar amounts of 4-chlorobenzaldehyde (2 mmol) and malononitrile (2 mmol) are stirred in water at room temperature. After 4 hours of stirring a precipitate is obtained which is filtered with water. The solid obtained is recrystallized from ethanol. The characterization of the compound corresponds to the data reported in the literature. Figure 2 shows the reaction scheme of the compound studied.

![Figure 2. Syntesis of 2-(4-clorobencilidene) malononitrile.](image)

The Z-scan experiment was performed using a frequency-bent Nd: YAG laser emitting at 532 nm, focused by a lens of focal length of 10 cm and with a waist radius of 40 microns; the system generates automated pulses; The cell used to contain the diluted sample is 1 mm thick. The transmission of the beam obtained in closed and open cell configuration is collected towards a detector.

3.2. Computational

We used the software Gaussian09 revision A02 [13] to carry out quantum-chemical calculations and GaussView 5.08 [14] as a visualizer. The optimization of the geometry was performed at the calculation level M062X/6311 + + G (d, p). Once the molecule was optimized, static linear and nonlinear optical properties, dipolar moments ($\mu$) polarizability ($\alpha$), first order hyperpolarizability ($\beta$) and second order ($\gamma$) hyperpolarizability were calculate.

4. Results and discussions

4.1. Spectroscopic characterization visible ultraviolet spectroscopy (UV-vis)

Figure 3 shows the ultraviolet spectrum in THF, where the maximum visible absorption ($\lambda_{max}$) and the strength of the oscillator ($f$) were obtained for the only two excited states of the molecule. This theoretical approach makes it possible to elucidate that at 532 nm the molecule in question has minimal absorption, which allows the laser to be used to measure the Z-scan.
4.2. Properties of nonlinear optics (NLO)

Figure 4 shows the structure of the optimized molecule as well as the numbering of all its atoms. The blue, gray, green and white spheres represent nitrogen, carbon, chlorine and hydrogen respectively.

Figure 4. (a) Numeration of the atoms present in the 2- (4-chlorobenzylidene) malononitrile; (b) Optimization of the molecular structure of 2- (4-chlorobenzylidene) malononitrile obtained through the calculation level DFT / M06-2X / 6311 ++ G (d, p).

The properties of non-linear optics were evaluated in order to study their relationship with the molecular structure, due to the fact that introducing electroattractor or electropolymer groups to the molecule shows a change between the properties of non-linear optics. The polarizability of the π electron system is achieved by joining electro donor groups and electro acceptors at the beginning and end of the rings or ring systems, with this a charge transfer axis is created, therefore, the polarizability of a molecule is the measure of the ability to respond to an electric field and acquire a dipole electric moment.

The values obtained for the average polarizabilities are shown in Table 1, as well as the value of the anisotropy of the polarizability $\Delta \alpha$ (dependence of the molecular orientation with respect to an applied electric field) as a function of it’s tensors (force exerted on a surface of
the molecule) on the $x$, $y$, $z$ axes. The results obtained show that the polarizability ($\alpha_{\text{tot}}$) of the compound is a positive value, which indicates that there is no loss of optical linearity and therefore hyperpolarizability values are acceptable to say that the compound in question has characteristics of nonlinear optics. The aforementioned as a consequence of both the asymmetry of the compound and the elongation of the conjugate system of which it consists. The calculated anisotropy of the polarizability of the compound under study is $3.215 \times 10^{-23}$ esu, which means that when an electric field parallel or perpendicular to the molecular axis hits the molecule it distorts its electronic cloud easily by the presence of an ion close or a dipole. Having a hyperpolarizability value ($\beta$) of $1.562 \times 10^{-29}$ esu the compound would be a material with nonlinear optical response, this due to the delocalization of electrons along a conjugated skeleton and the asymmetry that occurs thanks to the two groups, one acceptor such as the cyano groups (CN) that would enter into resonance with the system, thus increasing hyperpolarizability and an electrowinning group such as the chlorine group (Cl) that makes a greater contribution by activating the ring, increasing its electron density towards the Ethylenidian group that is in a pseudopara position with respect to phenyl, creating a preferential load axis increasing its optical characteristics.

Table 1. Electric dipole moment ($\mu$), Molecular polarizability ($\alpha$), hyperpolarizabilities ($\beta$) and ($\gamma$) of 2-(4-chlorobenzylidene) malononitrile.

| Parameter              | 4ClD2MM | Urea  | p-nitroanilina |
|------------------------|---------|-------|----------------|
| $\mu_{\text{total}}$ (D) | 5.199   | 3.919 | 7.040          |
| $\alpha_{\text{prom}}$ ($\times 10^{-23}$ esu) | 2.194   | 0.5226 | 1.501          |
| $\Delta \alpha$ ($\times 10^{-23}$ esu) | 3.215   | 0.2812 | 1.719          |
| $\beta_{\text{tot}}$ ($\times 10^{-29}$ esu) | 1.562   | 0.5037 | 10.890         |
| $\gamma_{\text{tot}}$ ($\times 10^{-36}$ esu) | 40.86   | 3.090  | 13.400         |

4.3. Z-scan technique
A sample of 2-(4-chlorobenzylidene) malononitrile dissolved in THF was used to measure both the non-linear absorption coefficient ($\beta$) and the non-linear refractive index $\eta_2$ by the Z-scan technique. The sample moves along the trajectory of the beam, with variations of the intensity of the incident beam that result in distortion and changes in the transmittance of the beam that were probed by two detectors, open aperture and closed aperture detectors. For all Z-scan measurements, a Nd: YAG laser was used, duplicated at an emission frequency of 532 nm and focused by a 10 cm lens, a 40-micron waist at the focal point, the radius of the waist of the laser beam is 1 mm, as shown in Figure 5.
The non-linear absorption coefficient was determined using the open-aperture scanning traces \( z \), which are associated with the imaginary part of the non-linear third-order susceptibility \( \chi^3 \). A graph of the normalized transmittance is plotted along the y-axis and the position of the sample along the x-axis. Generally, when the sample approaches the focus of the laser beam, the transmittance measured in the detector increases or decreases to form a peak or valley.

Figure 6(a) shows the open aperture curve for the compound in consideration of different incident laser powers (30 mW, 40 mW, 50 mW, 80 mW and 100 mW). The behavior observed in the graph is of inverse saturation, so the coefficient of absorption \( \beta \) is positive. Figure 6(a) also shows a comparison Z-scan scan in an open cell configuration, for the different laser powers used. The appearance of the thermal effect on the 4ClD2MM for a laser power of 30 mW is lower, but has less non-linearity, the opposite occurs in the curve of 100 mW of laser power, where the thermal effect is greater compared to the other laser power, but this shows a better non-linearity. The thermal effect increases with increasing laser power. In addition, it is observed that near 100 mW the power curves suffer a widening that indicates that the thermal effect produced by the laser focused on the sample begins to be significant, this effect observed in the Z-scan curve.

![Figure 6. Normalized transmittance for Z displacement of 50 mm in open cell configuration (a), and closed cell configuration (b) for laser powers of 30 mW, 40 mW, 50 mW, 80 mW and 100 mW, 2-(4-chlorobenzylidene) malononitrile.](image)

The closed-configuration z-scan experiment was performed to measure the non-linear refractive index (\( \eta_2 \)). Non-linear refraction is the phenomenon in which the refractive index of the medium varies with the high intensity laser beam. The real part of \( \chi^3 \) is obtained by evaluating the values \( \chi^3 \).

The closed configuration is shown in Figure 6(b). In it, a peak is observed followed by a valley in the normalized transmittance, which in turn indicates that the sign of the refractive non-linearity is negative due to the self-defocusing of the light upon impacting the sample.

In Table 2 and Figure 7, the results of the different parameters measured at each power are shown, observing that in all cases, the magnitudes of said parameters increase as the power increases.
Table 2. Non-linear parameters of extra virgin olive oil obtained from power sweeps.

| Power (mW) | $\eta_2 \times 10^{-5}$ ($cm^2/W$) | $I_0 \times 10^{7}$ ($cm^2/W$) | $\beta \times 10^{7}$ ($cm^2/W$) | $Re\chi^{(3)} (\times 10^{-23})$ (e.s.u) | $Im\chi^{(3)} (\times 10^{-23})$ (e.s.u) |
|------------|----------------------------------|--------------------------------|---------------------------------|----------------------------------------|----------------------------------------|
| 30         | -7.643                           | 4.774                          | 3.356                           | -1.499                                 | 8.067                                  |
| 40         | -5.911                           | 6.366                          | 3.573                           | -1.595                                 | 8.587                                  |
| 50         | -5.320                           | 7.957                          | 3.839                           | -1.712                                 | 9.224                                  |
| 80         | -2.278                           | 12.732                         | 5.308 -2.372                    | 12.755                                 |
| 100        | -1.415                           | 15.915                         | 6.284                           | -2.808                                 | 15.109                                  |

Figure 7. Variation of (a) non linear refraction index, and (b) non linear absorption coefficient, depending on the laser power according to Table 2 for 2-(4-chlorobenzylidene) malononitrile.

5. Conclusions
From the standardized transmittance curves obtained from the Z-scan technique, it was possible to characterize the various non-linear optical parameters of 2-(4-Chloro-disyldiene) malononitrile, observing that each parameter increases as the laser power increases. From the theoretical study of ONL, it was possible to predict that the compound is a matter of presenting optical activity, so that in relation to urea, the result suggests a promising application in optical devices, as was experimentally proven through the Z-scan technique.

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