Análisis experimental de las propiedades ópticas no lineales de los derivados del 1-aril-3-(4-metoxifenil)-5-(Benzo(*d*)(1,3)Dioxol-5-yl)-2*H*-pirazolinas.

Experimental analysis of the nonlinear optical properties of 1-aryl-3-(4-methoxyphenyl)-5-(Benzo(*d*)(1,3)Dioxol-5-yl)-2*H*-pyrazolines derivatives.

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Artículo de investigación científica y tecnológica

***Resumen*—Se realizó un estudio experimental y teórico de las propiedades ópticas no lineales de dos derivados de las pirazolinas 1-Aryl-3-(4-Metoxifenil)-5-(Benzo(d)(1,3) Dioxol-5-yl)-2H-Pirazolinas basadas en el poder de excitación del láser, para establecer su uso potencial en la industria fotónica[1]. Estos compuestos ya sintetizados y caracterizados por espectroscopia UV-vis, en THF como disolvente, se sometieron a lecturas en el sistema Z-scan para determinar diferentes parámetros ópticos, como el índice de refracción no lineal (η2), el coeficiente de absorción no lineal (β) y la susceptibilidad electrónica de tercer orden (X (3)). Para estas mediciones se utilizó un láser Cd Nd: YAG que emite a 532 nm, un foco de una lente de 10 cm, un iris de 1 mm y una celda de 1 mm de longitud; Para apoyar los resultados experimentales se realizaron cálculos de mecano cuántico con el nivel de cálculo M06-2X / 6-31 G (2d). Este estudio permitió correlacionar el diseño molecular con las propiedades ópticas.**

***Palabras claves*— Óptica no lineal, Pirazolinas, refracción, susceptibilidad and Z-scan.**

***Abstract*—An experimental and theoretical study of the non-linear optical properties of two derivatives of 1-Aryl-3-(4-Methoxyphenyl)-5-(Benzo(*d*)(1,3)Dioxol-5-yl)-2*H*-pirazolines was carried out. Pyrazolines based on the excitation power of the laser, to establish its potential use in the photonics industry [1]. These compounds already synthesized and characterized by UV-vis spectroscopy, in THF as a solvent, were submitted to readings in the Z-scan system to determine different optical parameters, such as the non-linear refractive index (η2), the absorption coefficient nonlinear (β) and third order electronic susceptibility ($X^{(3)}$). For these measurements, a Cd Nd: YAG laser emitting at 532 nm, a focus of a 10 cm lens, a 1 mm iris and a cell with a length of 1 mm were used; To support the experimental results, quantum mechanical calculations were performed with the calculation level M06-2X / 6-31 G (2d). This study allowed to correlate the molecular design with the optical properties.**

***Index Terms*—Non-linear optical, Pyrazolines, refraction, susceptibility and Z-scan.**

I. INTRODUCTION

the manufacture of optoelectronic, mass storage and/or digital devices is subject to the use of inorganic compounds doped with heavy metals such as gold, palladium, platinum, silver, zirconium, which are really expensive and difficult to synthesize; therefore, alternatives are currently being sought in organic compounds with greater synthesized accessibility, good performance and long useful life. In fact, evidence of interest in industries and academic research on "push-pull" type organic materials, that is, molecules with an electron donor fragment (D) and another electron acceptor (A) covalently linked through a spacer; for applications such as optical communications, light conversion, optoelectronics, flexible logic circuits, and energy conversion [2]. The integral parts of the fiber optic transmission system are currently manufactured by rare earth doped semiconductors; these components are costly to manufacture and constrain the technology for unique applications, such as remote telecommunications [3].

Pyrazolines and their derivatives have many applications, such as in the biological [4], pharmaceuticals, and industrial fields due to their role as antioxidants and as possible optoelectronic materials; the last one due to the presence of conjugated systems (spacer) with delocalization of the π orbitals, which increases the probability of charge transfer processes taking place. In addition, the ability to incorporate substituents donors and charge acceptors; in such a way that they give it a greater electronic flow [5,6]. These characteristics make the derivatives of 1-Aryl-3-(4-

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Methoxyphenyl)-5-(Benzo(*d*)(1,3)Dioxol-5-yl)-1*H*-Pyrazolines like as show in the Fig. 1, Ideal candidates for non-linear optics applications [7,8].

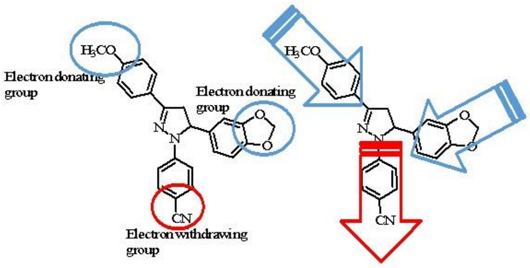


Fig. 1. Molecular structure and charge transfer pattern of substituted tri-aryl pyrazolines

Since the molecules studied are unpublished, an experimental study is included, carrying out a characterization by spectroscopic techniques; and computational under different levels of calculation to obtain its chemical and physical properties, in addition to predicting non-linear behavior against established patterns such as *p*-Nitroaniline and Urea based on results of variables known as the dipole moment (μ) , the polarizability (α) and the hyperpolarizability of the first and second order (β and γ) which use the components x, y, z; where β is the one that determines the optical non-linearity of the compound. (1-4) [9,10] were used to calculate these parameters.

The total static dipole moment (μ_{tot}), using the x, y and z components are defined as:

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

The average polarization (α_{tot}) which is defined as:

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

In first-order hyperpolarizability the components of β are defined as the coefficients on the Taylor series expansion of the energy in the external electric field when the external electric field is weak and homogeneous, this expansion is given below:

$$\beta = \sqrt{{\beta_x}^2 + {\beta_y}^2 + {\beta_z}^2} \qquad (3)$$

Therefore:

$$\beta_{tot} = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2\right]^{\frac{1}{2}} \quad (4)$$

A. *Z-scan technique*

It is a system made up of a laser, lens and detector in essence, as seen in Fig. 2, which provides information on the physical phenomena that a compound experiences when a current of photons impinges continuously, obtaining displacement values as a function to the percentage of transmitted light; With this numerical information, the value and sign of the nonlinear refractive coefficient η_2 are determined, as well as that of the nonlinear absorption coefficient β [11]. Similarly, electronic susceptibilities, which when they are higher than second order, are called nonlinear susceptibilities χ^3, which are the result of the cubic behavior of the susceptibility, thus causing nonlinear third order phenomena. . Third order nonlinear processes are generated when the incident electric field in the nonlinear medium is generally made up of three terms that oscillate at frequencies ω_1, ω_2 and ω_3. And the third order polarization of the medium is proportional to the cube of the incident field [12].

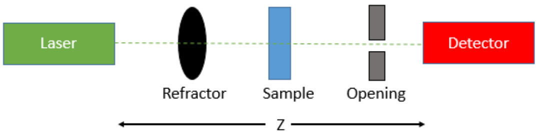


Fig. 2. Complete diagram of the Z-scan system

B. *Computational details*

Mechanical quantum calculations of polarizabilities (α, β and γ) were performed within the framework of the Density Functional Theory (DFT) using the functional M06-2X and the base set 6-31G (2d) established with the software revision Gaussian09 A .0212.

II. METODOLOGY

A. *Synthesis*

Fig. 3 show the precursor, (E)-3-(Benzo[d] [1,3] dioxol-5-yl)-1-(4-methoxyphenyl) prop-2-en-1-one, who it was first synthesized; a propenone aryl substituted, through a cross mixed aldol condensation, using equimolar amounts of Piperonal and Methoxyacetophenone in Ethanol at room temperature, with the addition of 50% NaOH, drop to drop [13]. After 2 hours of stirring a yellow-green precipitate is obtained, which is filtered and recrystallized from ethanol.

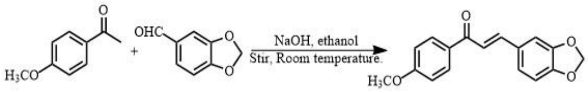


Fig. 3. Synthesis of (*E*)-3-(Benzo[*d*][1,3]dioxol-5-il)-1-(4-metoxifenil)prop-2-en-1-one.

This propenone was cyclized with phenylhydrazines suitably functionalized with the electron attracting groups CN and H, using methanol as solvent and glacial acetic acid as catalyst, under reflux conditions [14], until obtaining different solids depending of substituent groups, which were filtered and recrystallized from Methanol, Fig. 3 diagrams the synthesis of pyrazolines, where R is CN or H.

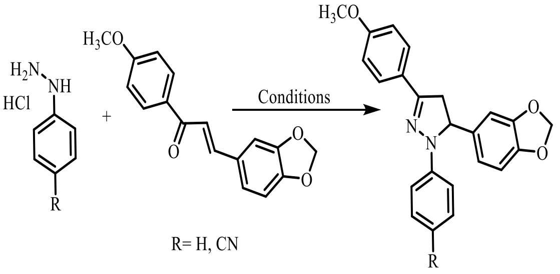


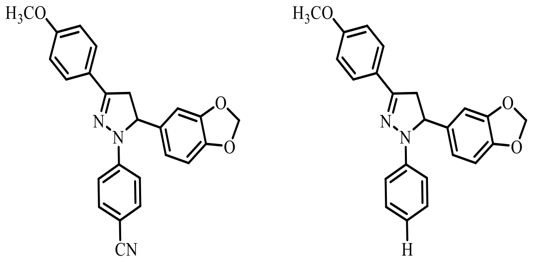
Fig. 4. Preparation of 5-(benzo[*d*][1,3]dioxol-5-yl)-3-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-2*H*-pyrazolines.

B. Z-Scan characterization

The Z-Scan experiment was performed using a frequency-doubled Nd: YAG laser emitting at 532 nm, focused by a lens with a focal length of 10 cm and a waist radius of 36 microns; the system generates automated pulses; the cell used to hold the diluted samples is 1 mm thick; the concentration was 0.1 M; varying the laser power from 10 mW to 150 mW. The transmission of the beam obtained in closed and open cell configuration is collected to a detector.

III. DISCUSSION AND RESULTS

A. Spectroscopic characterization



Pirazolina CN Pirazolina H

Fig. 5. Pyrazoline derivatives

Pirazoline CN: 4-(5-(benzo[d][1,3]dioxol-5-il)-3-(4-metoxifenil)-4,5-dihidro-2H-pirazol-1-il- benzonitrilo.
Pirazoline H: 4-(5-(benzo[d][1,3]dioxol-5-il)-3-(4-metoxifenil)-4,5-dihidro-2H-pirazol-1-il)Fenil.

Fig. 6 and 7 show the experimental ultraviolet spectra in liquid phase, dissolved in Tetrahydrofuran; where it was obtained that the maximum visible absorption (λmax) was 364 nm and 357 nm for Pyrazoline CN and Pyrazoline H respectively, this zone is where the transition from n to π^* characteristic of the free electron pairs of the nitrogen of the pyrazoline ring as evidenced in the research of *Elsherif et al* in 2014 [15]. Fig. 5 shows these structures, in addition to the null absorption at 532 nm, wavelength of the laser used for the analysis of the properties of nonlinear optics in this work.

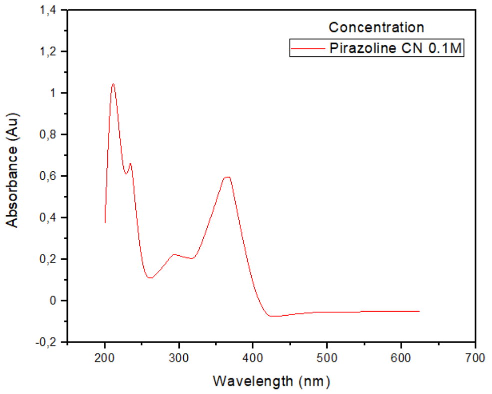


Fig. 6. Experimental UV-Vis spectrum of Pyrazoline CN

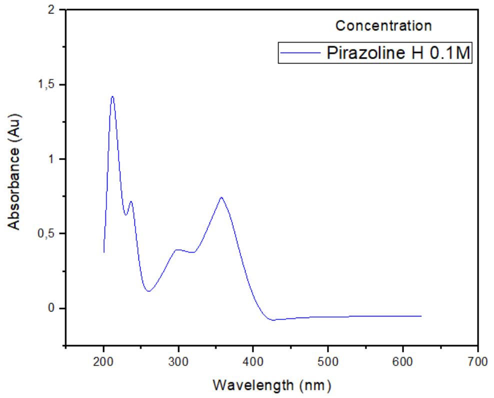


Fig. 7. Experimental UV-Vis spectrum of Pyrazoline H

B. Nonlinear Optical Properties

Experimental study using the Z-scan technique

A study was carried out based on the power of the laser, since it can be seen that when it varies, the sample shows a change in its properties; For this, a sample of each of the compounds was used at a concentration of 0.1 M in Tetrahydrofuran; Nonlinear refractive indices were determined, applying Snell's law (5 and 6).

$$\eta_{Air} \times Sin\theta_1 = \eta_o \times Sin\theta_2 \quad (5)$$

$$Sin\theta_1 = \frac{\eta_o}{\eta_{Aire}} \times Sin\theta_2 \quad (6)$$

$$y = mx + b$$

TABLE I.
LINEAR REFRACTION INDEX OF PYRAZOLINES

Pirazoline	Value (°)
CN	0,98358909
H	0,973186033

The laser powers used range from 10 to 150 mW; it was evidenced that in powers less than 20 mW a distinguishable transmission phenomenon is not observed; and at powers greater than 100 mW the solvent evaporates very easily, due to the thermal effect, which produces a change in concentration and the deviation of results. The readings made were made for both open and closed configurations respectively.

Fig. 8, 9 are the open configuration and shows two phenomena that are mainly due to the thermal effect that is caused by the increase in power in the laser, one that is characterized by the decrease in transmittance, and it is because the Spot of the laser is continuously focusing the sample, which leads it to act as a converging lens focusing the laser, which at certain low powers, causes a behavior in the graph with a band that rises and subsequently falls, which is attributed to a saturable absorption effect , which implies that to a certain extent the sample absorbs energy by the excitation of its electrons, but when it reaches the point that all its electrons are excited, the transmittance begins to increase, since the sample becomes transparent and allows light to pass through.

The phenomenon that occurs at higher powers in the open configuration is a displacement in the ΔTp-v which is a variable associated with the nonlinear refractive index, which will have positive or negative values depending on the behavior of the curve and the peak ratio - valley, where positive values are presented, when a graph is obtained in which a peak is presented first and then a valley, the difference will give positive results, which will make the non-linear refractive index a positive value, otherwise when the graph behaves with a valley and then peak, the difference would be a negative value, which indicates that the material produces auto-focus and / or auto-focus when irradiated with light, respectively, with this configuration the non-linear absorption coefficient was determined (β).

$$\beta = \frac{2(2\Delta T_{pv})^{\frac{1}{2}}}{I_0 L_{eff}} \quad (7)$$

Where I₀, is equivalent to (8) and joining them resulting in (9):

$$I_0 = \frac{P}{\pi\omega_0^2} \quad (8)$$

$$\beta = \frac{2(2\Delta T_{pv})^{\frac{1}{2}}\omega_0^2}{PL_{eff}} \quad (9)$$

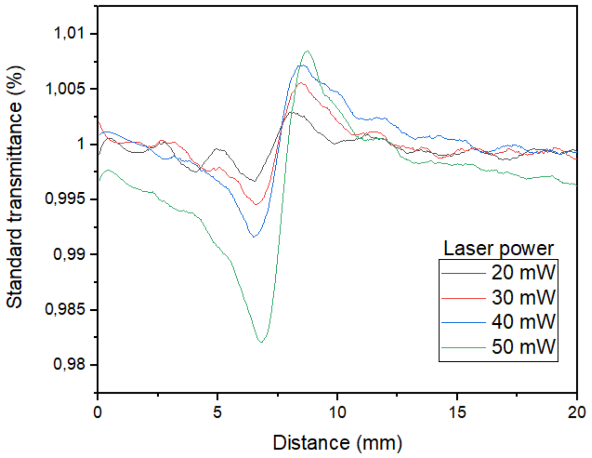


Fig. 8. Behavior according to the power of the Pirazolina CN, in open configuration. λ = 532 nm, Lens = 10 cm, L_{eff} = 0.1 cm.

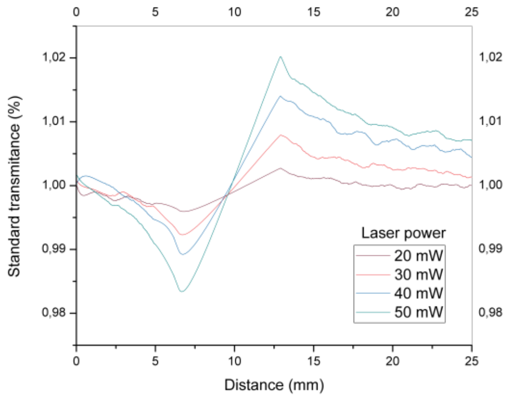


Fig. 9. Behavior according to the power of the Pirazolina H, in open configuration. λ = 532 nm, Lens = 10 cm, L_{eff} = 0.1 cm.

In Fig. 10 and 11 are the normalized transmittance curves for closed configuration, well-resolved curves are observed for each power, at low powers (40 mW) a decrease between the peak-valley distance is evident, however, the non-linear behavior is maintained. This is favorable because the materials in question do not need very high powers to distort their electronic cloud and present a non-linear response, which is explained taking into account the elongation and conjugation of the spacer system that governs its structure. The graphs also show a peak followed by a valley at normalized transmittance, indicating that the sign of refractive nonlinearity is positive due to auto blur. The non-linear effect begins around 4.0 and 7.5 mm respectively in Z, commonly for the different powers studied; it can be seen that as the laser power increases, ΔZp-v increases in addition to a widening in the peak-valley distance, in the lowest power (20 mW) it is where the self-defocusing thermal effect is best appreciated. As a product of the heating induced by the laser at the point where it is focused on the sample, a phenomenon is observed that is accentuated as power increases, since there is a decrease in transmittance and a displacement of ΔZ, this situation is framed from the start to finish on the Z-Scan curve; when presenting atoms with free electronic pairs such as Oxygen and Nitrogen, these molecules can be considered to cause different behavior in non-linear absorption and widening in the curve; the transmittance and displacement data, obtained with this opening mode, were used to obtain the non-linear refractive index (10) [16].

$$\eta_2 = \frac{\Delta T_{pv}\Delta Z_{pv}\lambda^2}{(2.7608)\pi PL_{eff}} \quad (10)$$

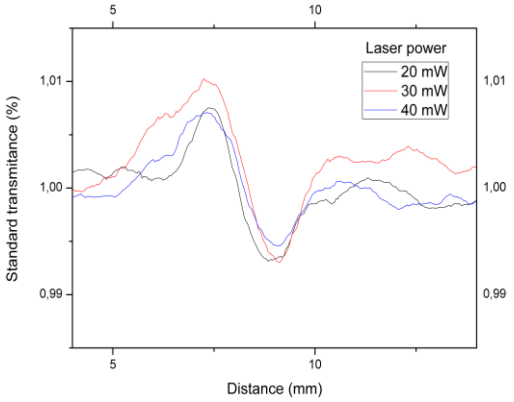


Fig. 10. Behavior according to the power of the Pirazolina CN, in close configuration. λ = 532 nm, Lens = 10 cm, L_{eff} = 0.1 cm.

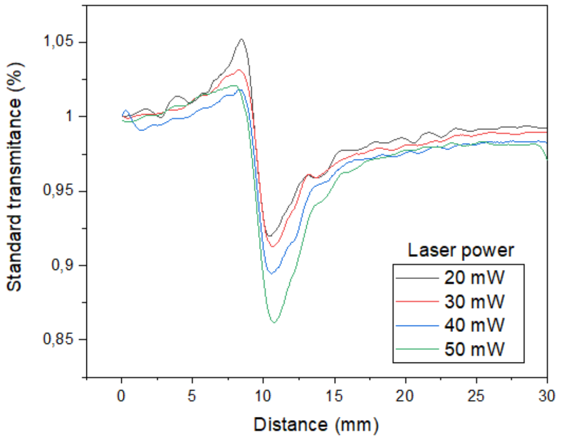


Fig. 11. Behavior according to the power of the Pirazolina H, in open configuration. λ = 532 nm, Lens = 10 cm, L_{eff} = 0.1 cm.

TABLE II.
VALUES OF B, H_2 Y X3 FROM NORMALIZED TRANSMITANCE CURVES, L_{EFF} = 0.1 CM PYRAZOLINE CN

P (mW)	**ΔT (cm)**	**ΔZ (cm)**	**I_0 (W/cm2)**	**B (cm/W)**	**n2 (cm2/W)**	**$\mathbb{R}\mathcal{X}^3$ (esu)**	**$\mathbb{I}_m\mathcal{X}^3$ (esu)**
20	0,00120877	0,102	491,217811	2,831x10^{-3}	2,012x10^{-4}	4,936x10^{-8}	1,737x10^{-5}
30	0,00142636	0,16	736,826717	2,050x10^{-3}	2,482x10^{-4}	6,092x10^{-8}	1,258x10^{-5}
40	0,00171996	0,184	982,435623	1,689x10^{-3}	2,582x10^{-4}	6,336x10^{-8}	1,036x10^{-5}
50	0,0028316	0,18	1228,04453	1,733x10^{-3}	3,326x10^{-4}	7,139x10^{-8}	1,063x10^{-5}
100	0,00313754	0,152	2456,08906	9,122x10^{-4}	1,556x10^{-4}	7,987x10^{-8}	5,597x10^{-6}

TABLE III.
VALUES OF B, H_2 Y X3 FROM NORMALIZED TRANSMITANCE CURVES, L_{EFF} = 0.1 CM PYRAZOLINE H

P (mW)	**ΔT (cm)**	**ΔZ (cm)**	**I_0 (W/cm2)**	**β (cm/W)**	**n2 (cm2/W)**	**$\mathbb{R}\mathcal{X}^3$ (esu)**	**$\mathbb{I}_m\mathcal{X}^3$ (esu)**
20	0,01325311	0,192	491,217811	9,374x^{-3}	4,152x^{-3}	8,917x^{-7}	5,033x^{-5}
30	0,01187211	0,236	736,826717	5,915x^{-3}	3,048x^{-3}	6,545x^{-7}	3,176x^{-5}
40	0,01239606	0,216	982,435623	4,533x^{-3}	2,184x^{-3}	4,691x^{-7}	2,434x^{-5}
50	0,01594406	0,272	1228,04453	4,113x^{-3}	2,830x^{-3}	6,079x^{-7}	2,208x^{-5}
100	0,02026092	0,332	2456,08906	2,318x^{-3}	2,195x^{-3}	7,992x^{-8}	1,245x^{-5}

The previous tables show the nonlinear parameters obtained at different laser powers; These values show in the first instance that as power increases, the nonlinear refractive index increases and the nonlinear absorption coefficient decreases progressively, for the two compounds; phenomena that according to their values are characteristic for materials with potential non-linear optical activity; This situation can be confirmed in turn by the results obtained with the Real Third Order Susceptibility (*Reχ3)* where the values range between 4,318x10^{-8} y 7,992x10^{-8} which are good since they are in the order of 10^{-7} y 10^{-9}, which was calculated together with its imaginary part, using the formulas (7 and 8); this behavior suggests that the molecules in question have a potential application in the photonics industry.

$$\mathbb{R}\mathcal{X}^3 = \left(\frac{10^{-4}\varepsilon_0 C^2\eta_0^2}{\pi}\right)\eta_2 \; (11)$$

$$\mathbb{I}_m\mathcal{X}^3 = \left(\frac{10^{-2}\varepsilon_0 C^2\eta_0^2}{4\pi}\right)\beta \; (12)$$

On the other hand, it can be interpreted that the presence or absence of electroattractor groups such as the Ciano (CN) group, causes variations in non-linear optical properties, since the transfer and flow of electrons is greater than when there is no group of this type, this occurs in compound B, which presents higher values for the nonlinear absorption coefficient and the nonlinear refractive index.

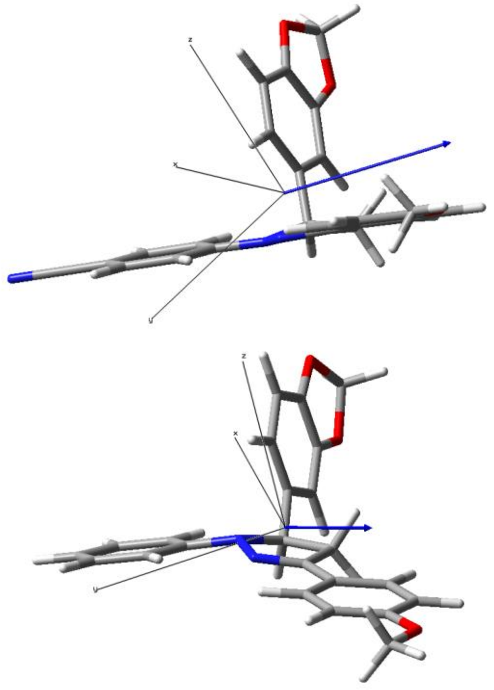
The results obtained for CN and H pyrazoline, in comparison to recent investigations Ayare NN et al in 2019, showed that the inclusion of electron withdrawing groups increases the value of electronic susceptibility and hyperpolarizability in 2 anthraquinones with values of 7.53 and 20.26 × 10-12 (m/W) for B and 1.81 and 3.50 ×10-13 (e.s.u) for X^3 [17], by making a comparison with a tri-arylsubstituted pyrazoline with 2 nitro groups and 1 hydroxyl group Janardhana et al in 2012, demonstrate the high values in electronic susceptibility and hyperpolarizability [18].

C. *Theoretical study using computational chemistry calculations*

For the theoretical determination of the non-linear optical properties of these molecules, it was used the Gaussian program in Windows environment using mechano-quantum calculations based on the density functional theory, with the functional M06-2X and the base set 6-31 G (2d), which showed good correlation with the experimental results, besides being reported in the bibliography as suitable methods to carry out these calculations in organic compounds such as sulfosalicylates [19], some dyes with fragments similar to the compounds under study [20].

The vector components of the calculated dipole moment are μ_x = -5.8587 D. μ_y = -6.0809 D and μ_z = -0.9768 D and the dipole moment is 8,5003 D;

graphically, the dipole moment vector indicates the route of charge transfer, showing once again that the benzodioxol group does not participate in said transfer due to the loss of conjugation. The polarizability of the π electron system is achieved by joining electron-donor and electron-acceptor groups at the beginning and at the end of the rings, thus creating a charge transfer axis, is can infer that it goes from the methoxyphenyl group to the cyano group, like show in fig. 12.



A. B.

Fig. 12. Cartesian coordinate system and dipole moment of A. pyrazoline CN B. pyrazoline H

TABLE IV.
DIPOLE MOMENT (M). POLARIZABILITY (A). HYPERPOLARIZABILITIES (B) AND (Γ) OF PYRAZOLINE CN AND H

Parameter	**Pirazoline CN**	**Pirazoline H**	**Urea**	***p*-Nitroaniline**
$\boldsymbol{\mu_{total}}$ (D)	8.5003	2.2074	4.025	6.3626
$\boldsymbol{\alpha_{ave}}$(x 10^{-23}esu)	4.61	4.22	0.4069	1.268
Δα (x 10^{-23}esu)	4.29	4.18	0.3269	1.701
$\boldsymbol{\beta_{tot}}$(x 10^{-30}esu)	15.11	7.13	0.4245	8.084
$\boldsymbol{\gamma_{tot}}$ (x 10^{-36}esu)	25.19	59.53	0.4569	6.111

The values obtained for the average polarizabilities are shown in Table 4, as well as the anisotropy value of the polarizability Δα (dependence of the molecular orientation on an applied electric field) as a function of its tensors (force exerted on a surface of the molecule) on the x-axes. and. z. It can be seen that the total polarizability values (αprom) result in a positive value ($4.61x10^{-23}$ and $4.22x10^{-23}$ esu, for pyrazoline CN and H respectively), which would indicate that there is no loss of optical linearity of the molecular system as a consequence of both the asymmetry of the compound and the conjugated system. The anisotropy of the polarizability of the compounds under study presents positive values, which means that when an electric field parallel or perpendicular to the molecular axis affects the molecule, it easily distorts its electronic cloud due to the presence of a nearby ion or a dipole. By having hyperpolarizability values (β) of $15.1x10^{-30}$ and $7.13x10^{-30}$ esu the compounds would be optimal materials with non-linear optical response, this due to the delocalization of electrons along a conjugated skeleton and the asymmetry that It is presented thanks to the electroattractor groups that would enter into resonance with the system, thus increasing hyperpolarizability, a case that is accentuated in the value of the Pirazolina CN, due to the presence of the CN group; but in addition the electronegativity and the lone electron pair of the oxygen (O) and nitrogen (N) atoms together with the extension of the π-electron bridge conjugation also leads to an increase in molecular hyperpolarizability. the values of βtotal obtained for the compounds under study have been compared with that of urea, which is a reference compound [21,22], which have a value of βtotal = $0.4245x10^{-30}$ esu determined at the same level of calculation . Having a value of β = 15.11 $x10^{-30}$ esu, Pyrazoline CN is 35.59, Pyrazoline H has a value of $\beta = 15.11\ x10^{-30}$ esu and is 16.79 times greater than that of urea, these results corroborate that the compounds are candidates to develop optoelectronic materials [23].

Blanco-Acuña EF et al in 2018, performed a theoretical study of the nonlinear optics properties of a triphenylpyrazole, performed under the cam-B3LYP/6-311++G(d,p) level of calculation, which presented interesting values of first and second order hyperpolarizabilities, taking into account that it is structurally similar with the study molecules of this work, which demonstrates that the presence of electron withdrawing groups (CN) improve such nonlinear optics properties [24].

IV. CONCLUSION

It was demonstrated with the Z-Scan measurements for the compounds Pirazolina CN and Pirazolina H, they present non-linear activity, since when exposed to the laser, they experience a variation in the transmittance curve, a phenomenon that is evident at 532 nm; in turn the values obtained for η_2, β and $Re\chi_3$, reflect a dependence of the power and are affected by the nature of the substituent group; since the presence of electroatrayectes groups like the Ciano group in the compounds exert variation in said properties, despite the fact that the same molecular skeleton is maintained for the compounds, this phenomenon was confirmed with the theoretical calculations in computational chemistry, comparing their non-linear optical properties. with each other and with standards such as urea, This result suggests a promising application in optical devices, in the photonics industry.

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REFERENCES

[1]. Prasad, P.N.; Williams, D.J. "Introduction to Nonlinear Optical Effects in Molecules and Polymers", John Wiley & Sons, New York, 1991.

[2]. S.R. Forrest, "The path to ubiquitous and low-cost organic electronic appliances on plastic", Nature 428, 911-918, 2004.

[3]. R.W. Boyd, "Nonlinear Optics", third ed; Elsevier publications, 2011.

[4]. T. Narender, K. Papi Reddy. "A simple and highly efficient method for the synthesis of chalcones by using borontrifluoride-etherate". Tetrahedron Letters, 48 (18) , 3177-3180, 2007.

[5]. Mao, S.S.H.; Ra, Y.; Guo, L.; Zhang, C.; Dalton, L.R.; Chen, A.; Garner, S.; Steier, W.H. "Progress toward Device-Quality Second-Order Nonlinear Optical Materials. 1. Influence of Composition and Processing Conditions on Nonlinearity, Temporal Stability, and Optical Loss", Chem. Mater., 10, 146-155, 1998.

[6]. Kang, H.; Facchetti, A.; Jiang, H.; Cariati, E.; Righetto, S.; Ugo, R.; Zuccaccia, C.; Macchioni, A.; Stern, C.L.; Liu, Z.; Ho, S.-T.; Brown, E.C.; Ratner, M.A.; Marks, T.J. "Ultralarge Hyperpolarizability Twisted π-Electron System Electro-Optic Chromophores: Synthesis, Solid-State and Solution-Phase Structural Characteristics, Electronic Structures, Linear and Nonlinear Optical Properties, and Computational Studies". Am. Chem. Soc., 2007, 129, 3267-3286.

[7]. Shi, Y.; Zhang, C.; Zhang, H.; Bechtel, J.H.; Dalton, L.R.; Robinson, B.H.; Steier, W.H. "Low (Sub-1-Volt) Halfwave Voltage Polymeric Electro-optic Modulators Achieved by Controlling Chromophore Shape". Science 07 Apr, Vol. 288, Issue 5463, pp. 119-122, 2000.

[8]. Agrawal, G.P.; Flytzanis, "Delocalization and superalternation effects in the nonlinear susceptibilities of one-dimensional systems". C. Chem. Phys. Lett., 44, 366-370.1976.

[9]. Oudar, J.L.; Chemla, D.S. "Hyperpolarizabilities of the nitroanilines and their relations to the excited state dipole moment". J. Chem. Phys., 66, 2664-2668, 1977.

[10]. H.A. Kurtz, J.J.P. Stewart, K.M. Dieter. "Calculation of the nonlinear optical properties of molecules". J. Compd. Chem. 11, 82–87, 1990.

[11]. A. Hormaza. A. O. Arbelaez. N. Montes. "Síntesis y caracterización espectroscópica de una serie de chalconas". Scientia et Technica Año XV, No 43, ISSN 0122-1701, 2009.

[12]. B. Insuasty-Obando. "Las chalconas y su uso como precursores en la síntesis de compuestos heterocíclicos nitrogenados". Rev. Acad. Colomb. Cienc. Ex. Fis. Nat. 40 (155): 234-243, 2016.

[13]. E. Mathew. V. Salian, I. Hubert Joe. B. Narayana. "Third-order nonlinear optical studies of two novel chalcone derivatives using Z-scan technique and DFT method". Optic and Laser Tecnology 120, 105697, 2019.

[14]. [Robert W. Boyd, "Nonlinear optical properties of a gold-silica composite with high gold fill fraction and the sign change of its nonlinear absorption coefficient". Journal of the Optical Society of America B Vol. 25, Issue 6, pp. 945-950, 2008.

[15]. Khaled Muftah Elsherif, Ashraf El-Hashani, Abdelmeneim El-Dali, Otman Dakhil, Adel Najar And Mohamed Algeriani. "Absorption Spectral Studies on Naphthyl Pyridyl Pyrazole (NPP) in Mixed Solvent Systems". Chem Sci Trans., 3(3), 1221-1227, 2014.

[16]. Geoffey New, "Introduction to Nonlinear Optics", cambridge university press, 2011.

[17]. Ayare NN, Ghanavatkar CW, Sreenath MC, Chitrambalam S, Joe IH, Sekar N, "Z-scan and DFT approach for investigating the NLO properties of imidazole fused anthraquinone dyes". Journal of Photochemistry and amp; Photobiology, A: Chemistry, 2019.

[18]. K. Janardhanaa, V. Ravindracharya, P.C. Rajesh Kumara, Umesh Gb, K. Manjunathab and Ismayil. "Nonlinear Optical Studies of a Novel Pyrazoline". AIP Conf. Proc. 1447, 1261-1262, 2012.

[19]. B. B. Ivanova, M. Spiteller. "Physical optical properties and crystal structures of organic 5-sulfosalicylates – Theoretical and experimental study". J. of molecular structure 1003, pages 1-9, 2011.

[20]. D. R. Mohbiya, N. Sekar, "Electronic structure and spectral properties of indole based fluorescent styryl dyes: Comprehensive study on linear and non-linear optical properties by DFT/TDDFT method". Computational and Theoretical Chemistry 1139, 90-101, 2018.

[21]. F.Q. Meng, M.K. Lti, S.J. Zhang and J. Chen. "Linear and nonlinear optical properties of a novel material: Urea-(DL)tartaric acid single crystal (UDLT)". National Key Laboratory of Crystal Materials, Shandong University, Jinan, 250 100, P.R. China. Volume 31, Issue 7, July, Pages 761-765, 1996.

[22]. U. Korkmaz, A. Bulut. "Synthesis, an experimental and quantum chemical computational study of a new nonlinear optical material: 2-Picolinium hydrogensquarate". Synthesis, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 130, 376–385, 2014.

[23]. Blanco-Acuña EF, Pérez-Hincapié L, Pérez-Gamboa A, Castellar-Ortega G, Cely-Bautista M. "Estudio computacional

conformacional, espectroscópico, ONL, HOMO–LUMO y reactividad de 1,3,5-trifenilpirazol". rev.ion. 31(2): 51-66. 2018.

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