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Second harmonic generation in pyrazoline derivatives of dibenzylideneacetones and chalcone: A combined experimental and theoretical approach

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Graphical abstract



Highlights

- Second-order nonlinear response of three pyrazoline compounds was investigated.
- The inclusion of pyrazole group increases the first-order hyperpolarizability.
- Pyrazolines powdered crystals are up to 5 times more efficient than KDP for SHG.
- Minor changes in molecular and crystalline structures influence strongly the SHG.

ABSTRACT

In this work, we investigate theoretically and experimentally second harmonic generation (SHG) in three pyrazoline compounds, being two derivatives of dibenzylideneacetone (DBA) ($C_{23}H_{20}N_2$ and $C_{25}H_{24}N_2O_2$) and one derivative of chalcone ($C_{21}H_{18}N_2$). The compounds were synthesized after two steps employing a Claisen-Schmidt condensation followed by an addition-elimination reaction with phenylhydrazine. All compounds were characterized using NMR, FT-IR, UV-Vis, and XRD. We calculated the first-order hyperpolarizabilities of these molecules using program packages based on the time-dependent Hartree-Fock (TDHF) and density functional theory (DFT). SHG was characterized by Kurtz and Perry's powder method. We observed that these organic crystals present SHG efficiencies up to 5 times larger than the KDP, and we associated these values to their molecular structure and crystalline arrangements. The values obtained experimentally and theoretically evidence that these compounds have good potential for application in electronic devices based on second-order nonlinear responses.

Keywords: Pyrazoline, Second harmonic generation, First hyperpolarizability, Hartree-Fock, density functional theory.

1. Introduction

Organic molecules (OM) have been systematically investigated as promising materials for nonlinear optics applications [1,2]. In comparison with inorganic compounds, OM present various advantages, including its low production cost, ease of synthesis, the possibility of device integration, high damage threshold, wide transparency range and intense optical nonlinear

responses [3,4]. The origin of the large optical nonlinearities in OM is related to the presence of π -electrons in their structure and the strong charge delocalization along the length of the conjugate system that they create [5].

Among the multitude of nonlinear effects, there was massive interest in the development of inorganic [6–8] and organic [9–13] materials with efficient second-order optical nonlinear responses, such as second harmonic generation (SHG). Indeed, since 1970s, a considerable increase on the SHG from organic compounds was observed exploiting dipolar and multipolar molecules [14–16].

The microscopic origin of nonlinear optical effects can be described in terms of the induction of a dipole moment due to the interaction of a molecule with an intense optic field. In this case, this dipole moment presents a nonlinear dependence with the excitation electric field described as

$$\boldsymbol{\mu} = \mu_i^0 + \alpha_{ij} \, \boldsymbol{E}_j + \beta_{ijk} \, \boldsymbol{E}_j \boldsymbol{E}_k + \gamma_{ijkl} \, \boldsymbol{E}_j \boldsymbol{E}_k \boldsymbol{E}_l + \cdots.$$
(1)

In this equation, the subscripts i, j, k refer to the spatial coordinates of the molecular systems; E_j , E_k , E_l are the vector components of the applied electric field; μ_i^0 is the molecule's permanent dipole moment; α_{ij} is the linear polarizability; β_{ijk} is the first hyperpolarizability, which is associated with the second-order nonlinear effects; and γ_{ijkl} is the second hyperpolarizability, that is related to third-order nonlinear phenomena [17].

Nevertheless, for nonlinear optical applications in which solid state materials, such as macroscopic organic crystals, are required, the medium response due to the interaction with an intense optical field is described by the nonlinear polarization

$$\mathbf{P} = P_0 + \chi_{ij}^{(1)} \mathbf{E}_j + \chi_{ijk}^{(2)} \mathbf{E}_j \mathbf{E}_k + \chi_{ijkl}^{(3)} \mathbf{E}_j \mathbf{E}_k \mathbf{E}_l + \cdots.$$
(2)

Here, P_0 is the static dipole moment, $\chi^{(1)}$ is the linear susceptibility, $\chi^{(2)}$ corresponds to the second-order nonlinear susceptibility, $\chi^{(3)}$ is the third-order nonlinear susceptibility.

Naturally, equations (1) and (2) are linked. The components of tensor $\chi^{(N)}$ are related to their molecular polarizability and hyperpolarizabilities counterparts through the molecules' organization in the crystalline structure. In summary, the susceptibilities values depend on the

way the molecules pack to form the crystal lattice and on the internal geometry of the individual molecule. For second-order nonlinear optical phenomena, such as SHG, the tensor elements of the macroscopic second-order susceptibility are represented by a sum of the molecules' first hyperpolarizabilities over the crystal unit cell

$$\chi_{IJK}^{(2)} = \frac{1}{V} f_I f_J f_K \times \sum_s \sum_{ijk} \cos \theta_{Ii}^s \cos \theta_{Jj}^s \cos \theta_{Kk}^s \beta_{ijk}$$

(3)

where V is the volume of the unit cell, f_I , f_K and f_K are tensors related to the local field corrections; the indexes *I*, *J*, *K* correspond to the crystallographic axes, while the molecular axes are labeled as *i*, *j*, *k*; *s* denotes the index of an equivalent position of a molecule in the lattice; θ_{Ii}^s is the angle between the crystallographic axis *I* and the molecular axis *i*_s [1,14].

By enhancing the NLO response at the molecular level, it is possible to achieve better macroscopic nonlinear properties through appropriate molecular engineering. Typically, enhanced molecular NLO can be achieved exploiting organic dipolar systems whenever strong electron donor (D), and acceptor (A) groups are inserted at the end of a π -conjugated bridge. These "push-pull" (D- π -A) organic molecules allow charge transfer to occur from one end to the other of the molecular structure, contributing to achieving higher values of the first-order hyperpolarizability [10,11,15]. However, dipolar molecular structures usually form centrosymmetric crystals, and this has been one of the much-reported problems of active SHG materials synthesis [9].

Branched molecular structures have been synthesized as an alternative molecular design to achieve a better performance of second-order nonlinear optical properties. These systems have quadrupolar (A- π -D- π -A or D- π -A- π -D), octupolar ((D- π -A)₃) and dendritic structures ((D- π -A)_n), and efficient SHG can be obtained due to the formation of non-centrosymmetric crystals [5,9,10,16,18–20].

Nowadays, the adjustment of molecular structures has been one of the most popular approaches to the design of SHG organic materials [21–24]. In summary, the ideal material for

that purpose should display high values of the first-order hyperpolarizability, asymmetric load distribution, high degree of electronic delocalization, transparency in the region of emission of SHG and favorable crystalline packing for efficient SHG [9,25–29].

Several classes of organic compounds present the abovementioned properties. Among them, pyrazolines are a class of organic compounds with a still poorly exploited potential aiming nonlinear optical applications. They contain C=N-N group in their structures and are related to ketones and aldehydes [30,31]. Pyrazolines are reduced dihydro [4*H*, 5*H*] pyrazole compounds in which have two adjacent nitrogen atoms in a ring of five members. This class of organic compounds is a versatile moiety that exhibits a wide variety of biological activities as antimicrobial [32], antioxidant [33], antidepressant [34,35], anti-inflammatory and analgesic [36,37], anticancer [38], antitubercular [39], antimalarial [40], antidiabetic [41], antiviral [30,42], anti-amoebic [43] and anticonvulsant [44,45]. Due to their structural versatility and capability to accept and donate electrons throughout the length of the π -conjugated systems, these compounds' second and third order nonlinear optical responses can be improved and are promising materials in optoelectronics and photonics technologies [46–55].

In this work, we investigated theoretically and experimentally the nonlinear optical response of three pyrazoline compounds. Two compounds are derivatives of dibenzylideneacetone (DBA), while the other one is a chalcone derivative. As a strategy to optimize their nonlinear responses, we theoretically calculate the value of the first-order hyperpolarizabilities of these molecules and analyzed the influence of: (i) changing the functional group C=O by C=N-N with the addition of the phenyl group linked to the nitrogen atom *sp*³ hybridized and (ii) the inclusion of donor group OCH₃ in the *para*-position of the pyrazoline derivative from DBA. Crystals of these compounds were synthesized and characterized by NMR, FTIR, XRD and UV-VIS absorption. We experimentally evaluated the SHG efficiency of these organic crystals in powder form.

2. Computational study

The molecules' dipole moment, as well as static and dynamic first-order

hyperpolarizabilities, were calculated using time-dependent Hartree-Fock (TDHF) and density functional theory (DFT). For TDHF calculations, MOPAC 2016 and GAMESS software were employed (the TDHF calculations with GAMESS were done on the geometries obtained with the ORCA program), while DFT was implemented using the Gaussian16 program package [56– 59]. Different functionals and basis set were exploited in this work. Applying this methodology, we intend to predict theoretically the influence of different molecular structures to the compounds' electrical properties, independently the computational method employed.

In this approach, the tensorial nature of the molecular dipole moment and hyperpolarizabilities is considered, and all tensor elements are provided. However, we will focus the analysis on the total values of these quantities, which have a direct relation with the respective tensor elements. The molecule's total dipole moment was calculated using the relation [1,60]

$$\mu_{\text{tot}} = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} , \qquad (4)$$

while the total first hyperpolarizability was evaluated as

$$\beta_{\text{tot}} = \sqrt{\left(\beta_{\text{xxx}} + \beta_{\text{xyy}} + \beta_{\text{xzz}}\right)^2 + \left(\beta_{\text{yyy}} + \beta_{\text{yzz}} + \beta_{\text{yxx}}\right)^2 + \left(\beta_{\text{zzz}} + \beta_{\text{zxx}} + \beta_{\text{zyy}}\right)^2}.$$
 (5)

In these equations, μ_i and β_{ijk} are the tensor elements of the dipole moment and first hyperpolarizability in the molecule's reference system.

In the present study, the molecules were drawn on the ChemDraw software [61] and preoptimized using Avogadro program [62]. From Avogadro's results, we extracted the input files to perform a new structural optimization. In the following procedures, all quantities were calculated considering the molecules in the gas phase.

Using the MOPAC 2016 software, the geometry optimization, as well as the entire calculation of the electric properties of all compounds, were done with the PM7 Hamiltonian. Then, the molecule's total dipole moment, μ , static first hyperpolarizability, $\beta(0; 0, 0)$, and

dynamic first hyperpolarizability, $\beta(-2\omega; \omega, \omega)$, were achieved with the TDHF method. The command POLAR (E = 1.16526 eV) was used in the calculation of the dynamic first hyperpolarizability, which is equivalent to consider that the wavelength of the fundamental optical field is 1064 nm. Such a procedure allows the comparison of the theoretical results with the experimental characterization, which was performed using a Nd:YAG laser.

With ORCA software, geometry optimizations for all the molecules were done with the PBE functional and the def2-SVP basis set using the resolution of identity approximation. Following this step, the calculation of electric properties of molecules was done with the GAMESS program also using the TDHF method with the double-zeta basis set augmented with d polarization functions on the heavy atoms (DZ+P(d)).

Using Gaussian16 program package [58], the equilibrium geometries of the model molecules were optimized using three distinct functionals, B3LYP, CAM-B3LYP and M06-2X, and the same basis set, 6-311++G(2d,p). Then, the same functionals and basis set levels of theory were employed to calculate the abovementioned electrical properties of the optimized structures, using DFT method.

3. Experimental

The chalcone and dibenzylideneacetones were synthesized by a Claisen-Schmidt condensation and they were converted pyrazolines by an addition-elimination reaction with phenylhydrazine on the carbonyl carbon. This is schematically shown in figure 1. The characterization of SHG exhibited by these compounds was performed employing the Kurtz and Perry powder method. The other characterization techniques provided us with relevant information regarding the studied crystals, such as absorption wavelengths, energy gap, and XRD patterns.



Reactional conditions: a) benzaldehyde (or 4-methoxybenzaldehyde), 1.1 (or 2.2) equivalent(s), respectively, NaOH, MeOH, H₂O; b) phenylhydrazine, H₂SO₄, MeOH, reflux.

Figure 1. Scheme of the synthesis of pyrazolines H-1, H-2 and H-3.

3.1. Procedures to the synthesis of the investigated compounds

3.1.1. Procedure for the preparation of dibenzalacetones DBA and DBA-OCH₃

To a solution of acetone (0.74 mL, 10.0 mmoles) and NaOH (880 mg, 22.0 mmoles) in ethanol/water 1:1 (50 mL) was added a solution of benzaldehyde (2.24 mL, 22 mmoles) in methanol (10 mL) at 0°C. The reaction mixture was then gradually allowed to reach room temperature under constant stirring. After 4 h, the formed solids were filtered, washed with a cold mixture of ethanol/water to yield the respective dibenzalacetone derivative in 89% yield (yellow crystals, 2.07 g, 8.8 mmoles). The same procedure was carried out for the synthesis of DBA-OCH₃, replacing benzaldehyde with 4-methoxybenzaldehyde (2.24 mL, 22.0 mmoles) to furnish it in 92% yield (yellow crystals, 2.70 g, 9.2 mmoles).

3.1.2 Procedure for the preparation of chalcone

To a solution of acetophenone (1.17 mL, 10.0 mmoles) and NaOH (440 mg, 11.0 mmoles) in ethanol/water 1:1 (50 mL) was added a solution of benzaldehyde (1.12 mL, 11.0 mmoles) in methanol (10 mL) at 0°C. The reaction mixture was then gradually allowed to reach room

temperature under constant stirring. After 4 h, the formed solids were filtered, washed with a cold mixture of ethanol/water to yield the respective chalcone derivative in 95% yield (yellow crystals, 2.00 g, 9.6 mmoles).

3.1.3 Procedure for the preparation of H-1, H-2 and H-3

To a solution of DBA (1.17 g, 5.0 mmoles) or DBA-OCH₃ (1.47 g, 5.0 mmoles) or chalcone (1.04 g, 5.0 mmoles) in 10 mL in ethanol was added phenylhydrazine (0.59 mL, 1.2 mmoles). To this solution was added, dropwise, a solution containing H_2SO_4 (98.1%, 0.27 mL, 5.0 mmoles) in 5.0 mL of ethanol. The reaction was kept at 60°C. After the reaction was over 5 hours, the solid formed was filtered and dried in a desiccator. The product was obtained as yellow crystals in 52% (0.84 g, 2.18 mmoles, H-1), 88% (1.70 g, 4.42 mmoles, H-2) and 82% (1.22 g, 4.09 mmoles, H-3) yields.

3.2. FT-IR analysis

Fourier-transform infrared (FT-IR) spectra were recorded on a Bomem FTR MB-102 spectrometer in the region of 4000-400 cm⁻¹ with KBr pellet, with 4 cm⁻¹ spectral resolution and a mean of 128 scans. Only significant peaks were recorded.

3.3. NMR analysis

¹H and ¹³C NMR spectra were recorded on a BRUKER 500 MHz Advance Spectrometer, located at the DQ-UFJF. As internal reference tetramethylsilane (TMS) or the residual signal of the CDCl₃ solvent was used. The chemical shift values (δ) were given in parts per million (ppm) and the coupling constants given in Hertz (Hz).

3.4. UV-Vis optical absorption

The compounds were dissolved in *N*, *N*-dimethylformamide (DMF) at a concentration equal to 10^{-5} mol/L⁻¹. The solution samples were conditioned in a glass cuvette with a 1 mm optical path, and the measurements were performed using a spectrophotometer UV-Vis (Agilent Cary

100 Scan, Varian). From the spectra, we calculated the energy band gap of the investigated pyrazolines crystals using Tauc relation [63].

3.5. Crystalline structure

The XRD powder patterns of the crystals was obtained using Bruker D8 Advance diffractometer with voltage 40 KV, current of 40 mA and a source of radiation Cuk α (λ = 1.54 A). The powder samples of the pyrazolines crystals were recorded in a range of 3-35 degrees 2-theta, with a stepsize of 0.02° and a steptime of 0.4 s per step with a solid-state detector comprising 192 channels of measurement.

3.6. Second-order nonlinear optical characterization

The experimental determination of optical susceptibilities in crystals is a laborious task. It usually requires the growth of a single crystal with good optical quality and large size, which can be time-consuming and costly. Aiming fast verification of SHG active materials, the method developed by Kurtz and Perry [64] is used as an alternative to measure the efficiency of new materials. In this methodology, the nonlinear optical materials were investigated in powder form.

This method is widely used to evaluate the potential of new materials for application based on SHG [15,22,25,27,65]. It consists of comparing the SHG intensity emitted by the investigated compound with the emission from a reference sample. As the emission from powdered samples is strongly affected by the particles size distribution, the thickness of the analyzed samples and light scattering, the measurements must be performed under the same experimental conditions.

Moreover, the investigation of SHG as a function of particle size is a very useful tool, which allows classifying the nonlinear material into two distinct classes, crystals that present phasematching and those that do not have phase-matching [22,25,27]. According to Kurtz and Perry [64], when the material presents phase-matching, the SHG intensity increases with the increase in particle size reaching an approximately constant value when the powder particles are much

larger than the coherence length. While materials that do not have phase-matching, the SHG emission signal has a maximum when the particle size of the powder is equal to the coherence length.

In the present study, a Nd:YAG Q-Switched laser, emitting at 1064 nm, with 8 ns pulse width and 10 Hz repetition rate was used as the excitation source. A set of half-wave plate and polarizer was employed to allow continuous control of the laser power. The powdered samples were placed on the surface of a glass plate. The incident light beam was directed to the surface of the powder with an incident angle of 45°. The light emitted normally in respect to the sample surface was collected by a set of lenses and coupled to an optical fiber connected to a compact CCD spectrometer. Optical filters were used to eliminate the presence of the fundamental beam. The light intensity emitted at 532 nm was measured. As a reference material, we have used powdered potassium dihydrogen phosphate (KDP).

As a result of the synthesis method, the organic crystals were already produced in a powdered form. However, for NLO measurements, the organic crystals and KDP were pulverized into a fine powder and sieved in different particle size ranges (< 75, 75-106, 106-150 and > 150 μ m). The grain samples were standardized in different sizes. The powdered materials were compacted in a small disk and positioned in the sample holder and exposed to laser radiation. The SHG efficiency results were obtained by calculating the ratio between the emission intensity from pyrazoline samples and KDP.

4. Results and discussion

4.1. FT-IR spectra

The FT-IR spectra of DBAs and chalcone showed all characteristic absorption bands of their structures, as the stretch of the carbonyl group (C=O, 1655-1651 cm⁻¹), the α , β -unsaturated system *trans* disubstituted alkene (HC=CH, 970-990 cm⁻¹) and pyrazolines exhibit characteristic absorption bands spectra related to C=N and C–N moieties at 1510-1600 and 1310-1330 cm⁻¹, respectively (Supporting Information, Spectra 1, 4, 7, 10, 13 and 16).

4.2. NMR spectra

Nuclear Magnetic Resonance spectra allowed the unambiguous elucidation of the compounds molecular structure. The data obtained by the NMR analysis of the DBAs and chalcone, as well as the H-1, H-2 and H-3 pyrazolines, are in agreement with those described in the literature [66–70] and are presented in the Supporting Information. For example, we will describe the signals related to pyrazoline H-2.

The ¹H NMR spectrum of H-2 (Spectrum 17) showed two doublet of doublets (*dd*) relative to the diastereotopic hydrogens CH₂ of the ring pyrazoline at chemical shift in 3.00 and 3.69 ppm, which have coupling constant ${}^{3}J = 6.6$ and 16.8 Hz, respectively. Two singlets in δ 3.8 and 3.85 ppm are observed, signals corresponding to the homotopic methyl hydrogens that are part of the methoxyl group. The aromatic hydrogens were identified in the range of δ 6.75 to 7.45 ppm. In this same frequency range, we can also find two doublets at 6.63 and 7.12 ppm the olefinic hydrogens (CH=CH) with a coupling constant of ${}^{3}J = 16.3$ Hz, confirming the *trans* isomerism present in the structure. The chemical shift of these hydrogens occurs at higher frequencies than expected because they are especially disjointed because of the magnetic field induced by double-bond electronic currents and proximity to the aromatic ring, a phenomenon called magnetic anisotropy [71]. In the ¹³C NMR spectrum of H-2 (Spectrum 18), the 19 signals corresponding to all chemically non-equivalent carbons present in the structure were observed. Signals at δ 55.5 ppm are attributed to the carbons of the methoxy groups and those occurring at 42.6, 63.8 and 159.9 ppm are part of the pyrazoline ring (CH₂, CH, and C = N, respectively). On the other hand, the signals of the aromatic and olefinic carbons appear in the range of δ 113.5 to 159.2 ppm.

4.3. UV-Vis absorption

UV-Vis spectra of the pyrazoline's solutions are shown in Fig. 2. It is observed that these exhibit bands characteristic of the electronic transitions of the studied chromophores, that can be associated with transitions between states $n \rightarrow \pi$ and $\pi \rightarrow \pi^*$ [27,29,72]. The molecules H-1,

H-2, and H-3 exhibited very good transparency in the visible region, in the range of 450-800 nm. Their absorption bands are mainly in the ultraviolet region, presenting peaks centered at 385 nm, 386 nm and 363 nm for the samples H-1, H-2, and H-3 respectively. Their energy gap was also estimated. For samples H-1 and H-2, the energy gap was 2.93 eV and 2.92 eV, respectively. Sample H-3, on the other hand, presented a slightly higher energy gap, equal to 3.06 eV. In addition, these crystals present low molar absorptivity in the region of 532 nm. It must be emphasized that an efficient SHG material should have a broad transparency window around the emission wavelength [5,9]. Therefore, these results indicate that SHG will not be significantly affected by reabsorption processes when an optical beam from a Nd:YAG interacts with these crystals [27,73].



Figure 2. UV-Visible spectra of the pyrazoline compounds.

4.4. X-rays diffraction

The XRD powder patterns of the three samples are shown in figure 3. Such patterns presented a high degree of crystallinity, which indicates that well-defined crystalline structures were produced. After an extensive search in the crystallographic main databases, such as ICSD and CSD from Cambridge, we did not find a perfect match for molecules H-1 and H-2. This searching comprised stoichiometry, 2D and 3D structural search as well.

Nevertheless, for the H-3 sample, the obtained XRD pattern presented a very good agreement with a previously reported structure for the same compound (CCDC 145482). This is a non-centrosymmetric structure, which belongs to P2₁ space group. Using Rietveld analysis tools from TOPAS V.5 software, it was possible to refine sample H-3 XRD data and determine that this crystalline material has cell parameters a=8.9199 Å, b=5.8915 Å, c=15.5999 Å and β =93.44°, very close to the reported. This result is showed in figure S1 of the supplementary material.



Figure 3. Powder XRD graphs of pyrazoline crystals.

4.5. Nonlinear optical properties

4.5.1. Molecular geometry

The optimized molecular structures and their corresponding geometric parameters, obtained using distinct functionals and basis sets, are summarized in the Supporting Information Tables S1-S3. It was observed that despite the employed functional and basis sets, all optimized molecules presented a C_1 point group symmetry. Additionally, the insertion of the pyrazoline nucleus causes a shift in structural planarity in phenyl 2, conserving the planarity of the

remaining molecules in all investigated compounds and level of theory. These results can be easily visualized in figure 4, where it is presented the planar, lateral and front views of the three compounds structures calculated with CAM-B3LYP functional and 6-311++G(2d,p) basis set.

It should be mentioned that a molecular structure for the H-3 sample was proposed previously by Foces et al. [74]. Analyzing only the bonds related to the carbon linked to the pyrazoline group, the calculated results using M06-2X and PBE functionals present the best agreement with the structure reported in ref. [74].



Figure 4: Molecular structure of chromophores pyrazolines H-1, H-2 and H-3 obtained with the CAM-B3LYP functional using the 6-311++G(2d,p) basis set.

4.1.1 Calculation of the first hyperpolarizability

A summary of the calculated electrical properties for the pyrazoline compounds using TDHF and DFT methods is presented in Tables 1 and 2. It should be noticed that for different functional and basis set, the calculated values of the molecules' dipole moment differs slightly, with the exception of H-2 sample. For this compound, the calculated values of dipole moment using Hartree-Fock (HF) and M06-2X were roughly two times smaller than the results obtained using other functionals. This difference can be attributed to the discrepancies among the optimized molecular structures obtained by distinct functionals, as well as the differences among the implemented Hamiltonians in each method.

Table 1: Total dipole moment (in units of Debye) of the pyrazoline compounds calculated using distinct functionals and basis set in gas phase.

	NLO Pyrazolines		
Functional	H-1	H-2	H-3
B3LYP	2.59	5.17	2.57
CAM-B3LYP	2.74	5.26	2.60
M06-2X	2.63	2.56	2.54
HF	2.89	2.54	2.82
PM7	2.72	4.82	2.73

Firstly, we compare the H-1 sample with its DBA molecule counterpart, investigated by Sudha et al. [24]. Using the theory level HF/6-31G (d,p) and the density functional theory (DFT), they obtained a total dipole moment of 4.12 D, which is ~ 1.6 times larger than the H-1 values calculated in this present work. This indicates that the functional group modification changes the molecular dipole moment significantly.

A similar analysis was performed, comparing molecule H-3 and its chalcone base structure, reported by Abegão et al. [26]. The calculated values of H-3 dipole moment were similar to the previously reported value of the original chalcone molecule, 2.54 D [26]. Such values are

suggesting that the change of the functional group C=O by C=N-N-Phenyl affects very little the molecule dipole moment in this case.

However, owing to the discrepancies amongst the dipole moment of H-2 molecules calculated by distinct methods, a direct comparison with previous works and H-1 molecule should not be undertaken.

Table 2: Theoretically calculated static and dynamic first-order hyperpolarizability of the pyrazolines compounds in gas phase, expressed in units of 10^{-30} esu. The dynamic β was evaluated for $\lambda_{exc}=1064$ nm.

	NLO Pyrazolines					
Functional	H-1		H-2		H-3	
	β (0;0,0)	β(-2ω;ω,ω)	β (0;0,0)	β(-2ω;ω,ω)	β (0;0,0)	β(-2ω;ω,ω)
B3LYP	28.9	114.7	15.7	77.0	11.8	33.5
CAM-B3LYP	14.9	35.9	6.3	19.2	6.3	12.9
M06-2X	16.7	44.0	7.4	24.5	6.8	15.0
TDHF	11.3	26.5	4.1	13.4	5.1	9.3
PM7	9.7	52.4	7.8	44.1	7.8	35.1

As shown in table 2, regarding the differences between the employed theoretical models, it can be observed that the investigated molecules present relatively large calculated values of static and dynamic first-order hyperpolarizability. These results are comparable with the response of other promising organic molecules reported in literature, such as chalcones [26,29,75,76], DBAs [24,25,27,77,78], and different pyrazoline-derivatives [48,51,79–82].

Although different functional and basis sets led to distinct values of the molecules' static and dynamic first hyperpolarizabilities, general behaviors can be detected. For instance, in comparison with its DBA molecule counterpart investigated by Sudha et al. [24]. The values of the calculated first-order hyperpolarizabilities of H-1 pyrazoline are larger than the reported values for the base structure [20]. This result suggests that the change of the functional group

C=O by C=N-N-Phenyl increases the electronic delocalization along the molecule, providing larger second-order optical nonlinear responses.

An analogous result was achieved when a comparison between molecule H-3 and its chalcone base structure, reported by Abegão et al. [26]. In this previous investigation, they calculated the static and dynamic first hyperpolarizabilities of the chalcone molecule in gas phase and within a specific solvent. They reported static and dynamic first-order hyperpolarizabilities equal to 5.3×10^{-30} esu and 9.1×10^{-30} esu in gas phase. Again, the compound with C=N-N-Phenyl functional group presents slightly higher calculated hyperpolarizabilities values, despite the level of theory employed.

Nevertheless, a definitive conclusion cannot be made comparing sample H-2 with its corresponding DBA. Indeed, Ravindra et al. [25] and Shettigar et al. [77] have previously investigated the second-order nonlinear response of this DBA para-disubstituted by the OCH₃ electron donor group (*p*-methoxy dibenzylideneacetone). Using MOPAC 2007 with PM6 Hamiltonian, the calculated value of this molecule's dynamic first-order hyperpolarizability was 22×10^{-30} esu, in gas phase [25]. On the other hand, its experimental value was estimated as 9.9×10^{-30} esu [77]. Analyzing only the theoretical result obtained with the functionals B3LYP, M06-2X, and PM7, the change of the functional group increased the nonlinear response of H-2 compound. On the other hand, the conclusion was the opposite whenever CAM-B3LYP and TDHF level of theory were employed.

Comparing the DBA-derivatives molecules, all results indicate that the first-order hyperpolarizabilities of sample H-1 are larger than the values exhibit by sample H-2. This indicates that the inclusion of the OCH₃ group caused a significant decrease in the value of the first order hyperpolarizabilities. This indicates that insertion of the OCH₃ group on both sides of this pyrazoline compound is not a good strategy to enhance its nonlinearity, which is the opposite behavior of the observed in the corresponding DBAs base structures [25]. This suggests that the branched molecular structure of pyrazoline, in other words, the addition of

C=N-N-Phenyl, affects the charge delocalization in a different fashion than the C=O group of the corresponding DBA system [25].

Another interesting common result observed in all calculations is that the chalcone derivative pyrazoline, H-3, exhibit smaller first hyperpolarizabilities values than H-1 and H-2 DBA- derivatives compounds. Comparing the pyrazolines H-1 and H-3, the only difference between them is the presence of a double bond and an additional single bond in the DBAderivative compound. This result suggests that, at the molecular level, the DBA-derivative pyrazoline is more likely to present better values of the first-order hyperpolarizability in comparison with the chalcone-derivative pyrazoline. We believe that the extent of the conjugate chain affects the charge transfer (CT) and determines the efficiency of SHG. The larger the conjugate chain, the higher is the first-order hyperpolarizabilities of the pyrazolines [25,77].

4.5.2. Study of SHG powder efficiency

The SHG response of a material depends inherently on its structural and electronic properties [5,9–12]. Thus, to verify the efficiency of macroscopic SHG, one should consider factors such as average crystal size, crystal packing, transparency in the region of interest, and excitation laser intensity.

Firstly, we performed the measurement of the SHG signal with the powders as prepared. Thus, the samples consisted of particles with a wide range of sizes, and all of them contributed to the observed SHG signals. In Fig. 5, we present the emission spectra obtained for the samples H-1, H-2, and H-3, comparing with the KDP results. The emission of light with a narrow spectral width, precisely at half the wavelength of excitation at 1064 nm, was observed. Under the same excitation and signal collection conditions, compounds H-1 and H-3 showed higher SHG intensities than that obtained for the reference sample, while the compound H-2 emission of second harmonic intensity was lower than that emitted by the KDP. These results indicate that all samples must exhibit at least one phase with a non-centrosymmetric crystalline structure. Indeed, samples H-1 and H-2 showed well shape diffractograms, but no structure determination was possible based on the XRD results. Nevertheless, based on the SHG results,

we believe H-1 and H-2 powders must present a non-centrosymmetric crystalline structure or, at least, a mix of phases in which at least one of them must be non-centrosymmetric. Further investigation must be carried out aiming an accurate crystalline elucidation of these materials.



Fig. 5. Comparative powder SHG intensity spectrum of pyrazolines crystals with KDP. For all measurements, the excitation laser average power was 28 mW.

We defined the sample's relative SHG efficiency (η) as the ratio between the intensity emitted by this compound and the second harmonic intensity emitted by the reference sample under the same experimental conditions. From the results presented in Fig. 5, it is observed that the compounds H-1 e H-3 were more efficient for SHG than KDP. H-1 is approximately 1.6

times more efficient than KDP, while of H-3 presented a SHG efficiency about 2.72 times higher than the reference sample.

As the intensity of the SHG signal obtained by the powder method depends on the size of the particles, for a more accurate evaluation of SHG efficiency, the crystals were pulverized and separated into four sets of samples, each one containing particles with distinct size distributions, that is, particles with sizes < 75 μ m, within the ranges of 75-106 μ m and 106-150 μ m, and larger than 150 μ m. We measured the SHG and its corresponding efficiency for each set, in comparison with powdered KDP response with the same size distribution, under the same excitation and light collection conditions. The results are presented in Figure 6.













As we can see in Fig. 6, the compound H-1 showed SHG signal and efficiency higher than the KDP for all the size ranges explored in this study. We also verified that the SHG signal of the crystals of H-1 increases as the particle size is raised. This result suggests that the combination of the relatively high hyperpolarizability of the molecule, associated with favorable crystallization contributed to these crystals' good second-order nonlinear response.

Similarly, to the sample H-1, the crystalline powder of H-2 exhibited larger SHG signal for larger crystals' size. However, their SHG intensity and efficiency were lower than the results presented by KDP and H-1 samples, throughout the particle size range explored in our work. Although a less efficient SHG was expected for compounds H-2, based on the first order hyperpolarizability calculations, this is not enough to explain this huge reduction in the experimental crystal response. These results indicate that the inclusion of the electron donor group OCH₃ at *para* positions of the phenyl groups located at the ends of the base molecule H-1, combined with the crystalline structure formed, resulted in the strong suppression of the SHG observed in the crystals of H-2.

Although its calculated hyperpolarizability value was slightly lower than that of H-1, the crystalline powder of the compound H-3 presented the highest efficiency of SHG among the materials investigated in this study. In fact, its SHG efficiency was about 5 times greater than the KDP when particles of a smaller size than 75 μ m were used. We believe this is related to the distinct crystalline structures and molecular packing of the investigated compounds.

Additionally, the observed SHG signal for H-3 presented an apparent discrete maximum for particles of size comprised between 106 and 150 μ m. In principle, this result would suggest that these crystals could be classified as *phase-matchable* [64]. However, a more detailed study must be performed with particles discriminated in narrower size ranges and ranges with larger particles included, before we can safely state in what class of nonlinear medium these organics crystals belong.

A direct comparison between the experimental SHG of the investigated samples with other similar groups of organic crystals cannot be easily done, owing to the limitations of the employed experimental techniques. In Table 3, it is summarized the results obtained in the present work and the reported values for chalcone and DBAs base systems. It can be noticed that no SHG efficiency was reported for DBA and chalcone base structures. On the other hand, DBA derivative compound substituted by OCH₃ showed a measurable SHG, with an efficiency of up to 15.5 and 6 times larger than the response of urea [25,77]. From these results, we observed that the inclusion of C=N-N-Phenyl produced crystals with much better SHG responses than the DBA [65] and chalcone [15] base structures. Nevertheless, without further information concerning the experimental conditions of these previous works, it is not possible to compare accurately the results among H-2 its corresponding base structure [25,77].

Compound	SHG efficiency	$\lambda_{cut-off}$ (nm)	Reference
H-1	$2.27^{a} \pm 0.02$	442	This work
H-2	$0.06^{a} \pm 0.00$	442	This work

Table 3: Experimental SHG and UV-vis.

H-3	$2.62^{a} \pm 0.30$	420	This work
DBA	0	440	Vanchinathan et al. [65] and Rajasekar et al. [83]
DBA 4-OCH ₃	15.5-6 ^b	434	Ravindra et al. [25] and Shettigar et al. [77]
Chalcone	0	435	Zhao et al. [15]

a In comparison with KDP powder. The experiments were carried out with pyrazolines and KDP particles size within the range from 75 to 106 μ m.

^b In comparison with urea.

5 Conclusions

We investigated experimentally and theoretically the optical properties of three pyrazoline compounds derived from two DBAs and a chalcone. It was observed that these molecules are NLO active materials and present excellent macroscopic and microscopic efficiency for second harmonic generation. Based on the theoretical analysis, it was verified that the branched molecular structure of the investigated pyrazolines compounds enhances the molecules first hyperpolarizabilities in comparison with the linear molecular structure exhibited by the chalcone and DBAs counterparts. We also verified that the introduction of the donor group OCH₃ at para positions in the compound H-2 reduces molecular second-order nonlinear response in comparison to the compound H-1. Additionally, the comparison of H-1 and H-3 first hyperpolarizabilities results suggests that increasing the conjugation length enhances the molecular nonlinear response. From SHG macroscopic measurements, it was verified that H-2 and H-3 samples presented the lowest and the highest SHG efficiencies respectively. The huge difference among the SHG efficiencies among H-1 and H-2 samples and the best performance exhibited by H-3 crystalline powder cannot be explained based only on their molecular geometry and their first hyperpolarizabilities. Indeed, this indicates that the formed crystalline structure is playing an important role on the macroscopic SHG exhibited by these compounds. The results strongly suggest that these compounds are potential sources for new NLO materials, which can be designed to present enhanced optical properties aiming applications in nonlinear second-order optical devices.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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