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On the Potential as Nonlinear Optical Material of a New Chalcone Derivative and its Crystal and Topological Analysis

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Abstract

We report a study of the structural, optical and electrical properties of a new chalcone. Using the Møller-Plesset Perturbation and the Density Functional approaches, the dipole moment, linear polarizability and second hyperpolarizabilities were calculated in static and dynamic electric fields. The supermolecule approach was used to simulate the crystalline environment of our crystal and the linear refractive index. Lorentz local field correction factor and third order macroscopic susceptibility were calculated, and the effects of solvent media on the non-linear optical properties are also taken into account through the Polarizable Continuum Model. This chalcone is almost planar, except for slight rotations in its open-chain which allows electron delocalization. This is also confirmed by an intramolecular hydrogen bond formed between the carbonyl and amine groups. Interestingly, a good third order macroscopic susceptibility value of $13.31 \times 10^{-22} m^2 V^{-2}$ was calculated, which is even higher than those reported for related chalcone derivatives.

Keywords: NLO properties; Hirshfeld surfaces; Chalcone

Introduction

Chalcone is a class of compound obtained from natural or synthetic sources that can be considered as a precursor agent of flavonoids and isoflavonoids^{1–4}. The chalcones' synthetic production process normally occurs by Claisen Schmidt condensation, in which aromatic aldehydes are condensed with acetophenones^{5–7}. This compound class presents two aromatic rings connected through a three-carbon bridge with a keto carbonyl group and one α , β -unsaturation³. Studies have showed some biological activities associated with chalcones, such as antimicrobial, analgesic, antiplatelet, anti-inflammatory, anti-ulcerative, antimalarial, antiviral, anticancer, antihyperglycemic, antioxidant and antitubercular^{1,8–12}.

In addition, chalcones can be applied for other purposes, such as new materials, environmental demands and biological functions. Regarding materials, some chalcones have showed potential properties

of nonlinear optics, contributing to new material developments associated mainly with electronic engineering and other sciences^{13–16}. For example, Ali et al. (2017)¹⁷ characterized in his work the morphological and optical properties of chalcone thin films, with possible application for optoelectronics devices. The characterization process involved crystallographic analyses, a theoretical approach and other experimental data. Also, Maidur et al. (2018)¹⁸ and Patil et al. (2016)¹⁹ studied third-order nonlinear properties of two novel chalcone derivatives. Analogously, Chaudhry et al. (2017)²⁰ showed through computational study the potential nonlinear optical application of a novel chalcone. Many times, chalcones can be associated with other molecules like polymers and composite materials. Shetty, Raghavendra, and Dharmaprakash (2016)²¹ doped a chalcone with films of poly(methylmethacrylate) representing a good candidate for an optical power limiting application.

Considering the wide use of chalcones, computational analysis is an important tool used for describing and obtaining the molecular geometry in different media, such as solution or gas phase. Thus, theoretical calculations can be applied to estimate the physical chemistry properties, such as nonlinear optical (NLO) properties in different solvents. Indeed, this approach has been used in many studies. For instance, Shkir et al., (2018) ²² describes the theoretical second and third nonlinear optical properties of a novel D- π -A type chalcone derivative. Similarly, AlFaify et al. (2018) used computational methodologies to describe electronic, spectroscopic and nonlinear optical properties of 1-threoninium picrate (LTHP) molecule ²³.

In this sense, this paper aims to present the structural elucidation of a novel dimethoxy amino chalcone (DAC), as well its theoretical nonlinear properties. The molecular structure of the proposed chalcone was confirmed using Single Crystal X-ray Diffraction and spectroscopic analyses. Hirshfeld surfaces were used for an improved understanding of the supramolecular arrangement and intermolecular interaction. In addition, the electrical properties of DAC crystal were calculated by using the supermolecule method (SM) to simulate the crystalline environment polarization on a DAC isolated molecule.

Experimental and computational procedures

Synthesis and Crystallization

An ethanolic solution of sodium hydroxide 30% (w/v) (10 mL) was added in a flask along with 2-aminoacetophenone (2 mmol). The reaction system was stirred until complete dissolution of the acetophenone, then 3,4- dimethylmethoxybenzaldehyde (2mmol) was added to the mixture and the reaction accompanied by CCD (Scheme 1). At the end of the reaction, a small amount of hydrochloric acid 10% (v/v) was added to neutralize the system. The product was filtered and recrystallized by slow evaporation from ethanol as solvent.



Scheme 1: Synthesis of DAC

Crystallographic characterization

A well-shaped single crystal of DAC was selected from the glass vial after crystallization for the single crystal X-ray diffraction (SCXRD) experiment (Table 1). The crystal structure was elucidated based on Mo K α intensity data acquired on a Bruker-AXS Kappa Duo diffractometer. These intensity data, measured on a APEX II CCD detector, were processed using SAINT²⁴ and SADABS²⁴ before inputting them into the SHELXS-2014 ²⁵ program to solve structure with direct methods of phase retrieval. The initially solved model was refined using full-matrix least-squares on F² with SHELXL-2014²⁵.

1.2 U_{eq} (C_{sp}^{2} or N) or 1.5Ueq (C_{sp}^{3})] displacement parameters. Hydrogen positions were defined according to stereochemical assumptions and oscillated as the position of each bonded non-hydrogen atom. A summary of crystal data and refinement statistics of DAC is displayed in Table 1. Interpretation of the structure and graphical drawings were dealt with by MERCURY²⁶ and ORTEP-3²⁷.

where the second second

Structural formula	$C_{17}H_{17}NO_3$
Formula weight	283,32 u.a
Crystal system, space group, Z	Monoclinic, C2/c
	a = 31.262
Unit cell dimensions (A)	<i>b</i> =4.289
	<i>c</i> =25.694
	$\alpha = 90$
Unit cell dimensions (°)	$\beta = 121.75$
	γ=90
Volume (A ³)	2929.567
Calculated density (g/cm ³)	1.285
Absorption coefficient (mm-1)	0.088
Absorption correc. T_{min}/T_{max}	multi-scan T _{min} /T _{max} =0,542
F(000)	1200
Z	8
θ range for data collection (deg)	0.932-25.217
index ranges	-36 to 36
	-4 to 5
	-30 to 21
data collected	6787
unique reflections	2584
symmetry factor (R _{int})	0.0565
completeness to θ°_{\max} (%)	98.0
parameters refined	191
Goodness-of-fit on F^2	1.120
Final <i>R</i> indices $[I>2\sigma(I)]$	3.657
R_1 (all)	0.0844 (0.1165)
wR_2 (all)	0.2656 (0.3176)
largest diff. peak hole $(e/Å^3)$	0.235/ -0.267
CCDC deposit no.	1589863

Table 1: Crystal data and Refinement Parameters of DAC

Hirshfeld Surface Analysis

The Hirshfeld surface (HS) arose from an attempt to define the space occupied by a molecule in a crystal in order to partition the crystal electron density into molecular fragments^{28,29}. For this, a weight function for each atom in a molecule is defined as

$$w_a(r) = \frac{\rho_a^{at}(r)}{\sum_{i \in molecule} \rho_i^{at}(r)}$$

where $\rho_i^{at}(r)$ are spherically averaged electron densities of the various atoms. Then, the electron density of an atomic fragment can be defined as

where $\rho^{mol}(r)$ indicates the molecular electron density.

It is a powerful graphical tool for molecular interaction analysis, evaluating the electronic distribution in the environment external to the molecule³⁰. The dnorm surface evaluates the distances between atomic nucleus internal atoms and the HS (di) and the distance from the surface to the nearest atom in the molecule (de), normalizing them as a function of van der Waals radius.

Instead of plotting de and di on the Hirshfeld surface, contact distances are normalized in Crystal Explorer using the van der Waals radius of the appropriate internal and external atom of the surface³¹:

$$d_{norm} = \left(d_i - r_i^{vdw}\right) / r_i^{vdw} + \left(d_e - r_e^{vdw}\right) / r_e^{vdw}$$

The blue color indicates low intensity, and red color indicates high intensity of contacts. In addition, hydrophobic interactions are represented by shape index surface as large red and blue regions of concave and convex curvature. This surface is a measure of "which" shape, defined in terms of principal curvatures k_1 and k_2 :

$$S = \frac{2}{\pi} \arctan\left(\frac{k_1 + k_2}{k_1 - k_2}\right)$$

Shape index has the useful property that two shapes that differ by only a change of sign represent complementary pairs and, because of this, maps of shape index on the Hirshfeld surface can be used to identify complementary hollows (red) and bumps (blue) where two molecular surfaces touch one another²⁸.



Fig. 1: An outline of the bulk is displayed.

Powder Diffraction

The XRPD patterns of DAC were recorded using a XPERT PANalytical diffractometer with filtered Ka1 radiation of a Cu tube, operating at 40 kV and 45 mA, equipped with X'Celerator detector. To perform more accurate XRPD measurements 7 and 12 keV photons were used at XRD1 beam line of Brazilian Synchroton, at 100K and room temperature. All measurements were carried out in transmission mode holding the gently grind sample in 0.7 mm glass capillary. Procedures for the structural determination were performed by DASH³²(32)(31) (30) using the XRPD data and the molecular structure information obtained by NMR. To accomplish Rietveld analyses from CIF corresponding to single crystal data analysis Diffrac.suite TOPAS version 4.2 was used considering the Fundamental Parameters Approach (FPA).

Infrared and Raman spectroscopies

The infrared absorption spectra of DAC were obtained in KBr, ca. 1% solution, on FTIR/IR Affinity-1 Shimadzu spectrophotometer. Moreover, to correct the systematic overestimation of the vibrational frequencies, which is characteristic of the DFT methods³³, a scale factor of 0.958 was applied

in the theoretical values ³⁴. This provides more reliable values to compare to the experimental data from 2.6 NMR spectroscopy.

Raman spectra of different regions of a DAC crystal sample surface were collected with 20x objective lens at room temperature using a PeakSeeker 785 (RAM – PRO – 785) Raman system with a diode laser of 785 nm and 50 mW at the source. The backscattered Raman radiation was dispersed with a grating and focused on a Peltier-cooled charge-coupled device CCD detector allowing us to obtaining a spectral resolution of 6 cm⁻¹. All spectra were recorded at room temperature in the spectral window of (from 200 - to 2000) cm⁻¹ with same acquisition time (10 s).

NMR spectroscopy

All NMR experiments were run on a BRUKER, DRX400 MHz equipment at 9.4 T, in a BBO 5 mm probe, at 298 K, and TMS (tetramethylsilane) for internal reference. For 1H, 13C NMR, DEPT135 and HSQC, CDCl3 was used as solvent. The splitting of proton and carbon resonances was reported as s= singlet, d= doublet. ¹H NMR δ (ppm): δ 3.93 (s ; 3H ; 4-OMe) ; δ 3.95 (s ; 3H ; 5-OMe) ; δ 6.29 (broad single ; 2H ; -NH₂) ; δ 6,70 (m ; 2H) ; δ 6.89 (d ; 1H ; 8.36 Hz) ; δ 7.15 (d ; 1H ; 1.59 Hz) ; δ 7,22 (dd ; 1H ; 1.86 e 8.18 Hz) ; δ 7.28 (m ; 1H) ; δ 7.47 (d ; 1H ; 15.50 Hz ; C α) ; δ 7.69 (d ; 1H ; 15.50 Hz); δ 7.86 (m; 1H). ¹³C NMR δ (ppm): 191.7; 151.1; 150.8; 149.2; 143.1; 134.1; 130.9; 128.2; 122.7; 121.0; 119.3; 117.2; 115.8; 111.1; 110.0; 55.9.

To study the electrical properties of the DAC crystal we used the supermolecule method (SM) to simulate the crystalline environment polarization on a DAC isolated molecule. This approach works with a bulk consisting of a set of 11x11x11 unit cells, where each unit cell has 8 asymmetric units and each asymmetric unit has 38 atoms, creating a bulk with 404624 atoms; as can be seen in an outline in Figure 1, the isolated DAC is in the middle of the bulk with a blue outline. The atoms that surround the isolated molecule were considered as point charges.

Computational Methodology

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To study the electrical properties of the DAC crystal we used the supermolecule method (SM) to simulate the crystalline environment polarization on a DAC isolated molecule. This approach works with a bulk consisting of a set of 11x11x11 unit cells, where each unit cell has 8 asymmetric units and each asymmetric unit has 38 atoms, creating a bulk with 404624 atoms; as can be seen in an outline in Figure 1, the isolated DAC is in the middle of the bulk with a blue outline. The atoms that surround the isolated molecule were considered as point charges.

The SM approach was used in Ref.³⁵ to represent the dipole moment and the first hyperpolarizability with results close to the experimental ones. In Ref.³⁶, the authors calculated the macroscopic properties of the linear $\chi^{(1)}$ and second order nonlinear $\chi^{(2)}$ crystal susceptibilities for urea and thiurea, using the SM approach, and their theoretical results were close to the experimental ones. In Ref.³⁷ the authors also simulated the properties of $\chi^{(1)}$ and $\chi^{(2)}$ of the molecule 3-methyl-4-nitropyridine-1-oxide with results again close to the experimental ones.

The iterative process of SM is carried out in several steps: First we determined the electric charge of the isolated molecule, by adjusting the molecular electrostatic potential through a **CHELPG** fit, considering the electric charge distributions in vacuum through the MP2 method, using 6 - 311 + G(d) basis set ^{35,38}. The partial atomic charges of the single isolated molecule of an asymmetric unit are calculated by **CHELPG**. Then we replace each corresponding atom in the unit cells generated by the previously obtained partial atomic charge, and the static electric properties and the new partial atomic charges of the asymmetric unit are calculated. The iterative process continues with the substitution of the partial atomic charges in each calculation step, until the convergence of the electric dipole moment is reached; see Figure 2.



Fig.2. Evolution of values of the dipole moment of the DAC with the respective iteration numbers. Step 0 indicates the isolated molecule, and the other steps indicate the DAC crystal.

The components and the average values of electronic dipole moment (μ_i, μ) , molecular linear polarizability $(\alpha_{ij}, \langle \alpha \rangle)$ and anisotropy of linear polarizability $(\Delta \alpha)$ were calculated using the MP2 theory, and Density Functional Theory (DFT) at level *CAM* – *B3LYP* was employed for the calculation of the components and the average values of the second hyperpolarizability $(\gamma_{ijkl}, \langle \gamma \rangle)$. The set basis 6 - 311 + G(d) was used in both calculation methods.

The electrical parameters of the DAC crystal were calculated using the following expressions for the total dipole moment,

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{\frac{1}{2}},\tag{1}$$

average linear polarizability,

$$\langle \alpha \rangle = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3},\tag{2}$$

anisotropy of linear polarizability,

$$\Delta \alpha = 2^{-1/2} \left[\left(\alpha_{xx} - \alpha_{yy} \right)^2 + \left(\alpha_{yy} - \alpha_{zz} \right)^2 + \left(\alpha_{zz} - \alpha_{xx} \right)^2 + 6 \left(\alpha_{xz}^2 + \alpha_{xy}^2 + \alpha_{yz}^2 \right)^{1/2} \right]^{1/2}$$
(3)

first total hyperpolarizability,

$$\beta_{total} = [(\beta_{XXX} + \beta_{XYY} + \beta_{XZZ})^2 + (\beta_{YYY} + \beta_{YZZ}^{--} + \beta_{YXX}^{--})^2 + (\beta_{ZZZ} + \beta_{ZXX} + \beta_{ZYY})^2]^{\frac{1}{2}}, \tag{4}$$

and average second hyperpolarizability,

$$\langle \gamma \rangle = \frac{1}{15} \sum_{i,j=x,y,z} (\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji}).$$
⁽⁵⁾

Here the medium optical dispersion was not taken into account; therefore, the mean value (or absolute value) of the static second hyperpolarizability can be simplified by using the Kleinmann³⁹ approximation and calculated through the expression,

$$\langle \gamma \rangle = \frac{1}{5} \left[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2 \left(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz} \right) \right].$$
(6)

The relation between the average linear polarizability $\langle \alpha \rangle$ and the crystal linear refractive index (*n*) is given by the Clausius- Mossotti equation ⁴⁰, which is,

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N}{3} \langle \alpha \rangle,$$
(7)

where *N* is the number of molecules per unit cell volume. The third-order electric susceptibility $(\chi^{(3)})$ is related with the average second hyperpolarizability by the expression ⁴⁰,

$$\chi^{(3)} = f^4 N \langle \gamma \rangle, \tag{8}$$

where f is the Lorentz local field correction factor given by,

$$f = \frac{(n^2 + 2)}{3}.$$
 (9)

All the numerical results for the tensors' polarizability and hyperpolarizabilities were obtained from the Gaussian 09⁴¹ output file and converted by electronic units (esu).

For the theoretical calculations, the molecular geometries of DAC were carried out from the crystallographic information file (CIF). Then this geometry was fully optimized using the density functional theory (DFT) implemented in the Gaussian 09 package⁴¹, with the Handy and co-workers long-

range corrected version of B3LYP using the Coulomb-attenuating method, CAM-B3LYP⁴² as functional and, as basis set, we used the 6-311+G(d) of Pople and co-workers⁴³.

Results and discussion

Solid state characterization

The DAC compound, bearing two methoxy groups at 3',4'-positions of ring B and an amine group at 2-position of ring A, crystallized with one crystallographically independent molecule (Z' = 1) in a monoclinic space group C2/c (Z' = 8) (see Table 1 for a summary of crystal data). Its conformation does not differ much from those of the two polymorphs of the 3',4',5'-trimethoxy-2-amino analog ^{44,45}. Its molecule is almost completely planar, except for slight rotations on the three single bonds of the open-chain (C1–C7, C7–C8 and C9–C10), as Figure 3 shows.



Fig 3. 30% probability ellipsoid plot of DAC. Non-hydrogen atoms are arbitrarily labelled, and hydrogen atoms are shown as spheres of arbitrary radii. Colored area denotes the S₁¹(6) ring. This conformational feature can be viewed in the slight twist of 13.0(2)° between the two least-squares planes calculated through ring A (see Figure 3 for labeling scheme of chalcone rings) and through the propanone non-hydrogen atoms. The coplanarity between the central mean plane calculated through O1, C7, C8 and C9 and ring B is still higher (the bent angle between their least-square planes is

B and the propanone moiety, respectively (Table 2).

Torsion	DAC
C6-C1-C7-C8	14.3(7)
C6-C1-C7-O1	-168.5(5)
C2-C1-C7-O1	11.3(8)
C2-C1-C7-C8	-165.9(5)
C9–C8–C7–O1	9.1(8)
C9–C8–C7–C1	-173.5(5)
C8-C9-C10-C11	-9.1(8)
C8-C9-C10-C15	166.6(5)
C11-C12-O2-C16	1.2(7)
C13-C12-O2-C16	-178.9(4)
C12-C13-O3-C17	179.3(4)
C14–C13–O3–C17	0.1(7)

Table 2: Selected torsion angles of DAC

These two planarity deviations arose from the steric hindrance between vicinal hydrogen atoms bonded to C8 carbon and the carbons at the ortho-position of rings A and B⁴⁴. As a consequence of these planarity deviations, phenyl rings A and B are twisted by $19.18(16)^{\circ}$. Likewise, the torsion values on the C7–C8 bond axis evidenced a subtle coplanarity deviation in the propanone moiety (Table 2), as mentioned above. All torsions around this three-bond axis measure close to either 0° or 180°.

Contrary to the aforementioned trimethoxy analog, which is present with the methyl moiety of methoxy in the para-position, and is outside the phenyl ring B plane, both methyl groups of DAC are coplanar to phenyl ring B. Furthermore, an anti (also called s-cis) conformation around C7–C8 can be described compound for 1, which is preferred over the syn one in chalcone class ^{46–49}.

Concerning the non-covalent contact pattern, an intramolecular hydrogen bond is formed between the carbonyl and amine groups, assembling a $S_1^{1}(6)$ ring. The other amine hydrogen, which is not involved in this hydrogen bonded intramolecular motif, is engaged in bifurcated non-classical hydrogen bonds with both methoxy oxygens of a glide-symmetry-related molecule, giving rise to a $C_1^2(11)$ running along [001]. Interactions involving the amine and methoxy groups are also found in one of the two polymorphs of the 1-like compound present with one further methoxy moiety at 5-position of ring B.⁶ In the other polymorph, amine groups are intermolecularly involved only in N-H...**p** contacts⁵. In addition, two of these one-dimensional chains, growing in opposite directions parallel to the c axis, are cross-linked through a weak non-classical hydrogen bond between the carbonyl oxygen and the para-position methyl group of 2₁-screw axis symmetry related neighbors (Figure 4). This last contact, together with the chain motif, gives rise to a second level $R_2^3(9)$ motif made up of four hydrogen bonded molecules, constituting the main supramolecular entity of the crystal packing of DAC.



Fig 4. Crystal packing of DAC showing the chains running in the opposite direction along the [001] direction (framed). Only hydrogens involved in the shown contacts are displayed. H...A and D-H...A measurements are shown. Colored area denotes the $R_3^2(9)$ motif.

Hirshfeld surface (HS) analysis was used for an improved understanding of intermolecular interactions and their role in the supramolecular arrangement of DAC. The first approach involves the normalization of de and *d*i contacts on a unique surface named d_{norm} , showed in Figure 5 with the fingerprint plots for H-O contacts. By analyzing the red spots on the HS, it can be noted that the N1-H1A···O3 interaction is slightly stronger than the N1-H1A···O2 interaction (red spots more intense), which is confirmed by distances between donor and acceptor atoms (3.058 Å and 3.288 Å, respectively). In addition, H bonds are characterized on the fingerprints plots of Figure 5 as two pointed peaks, where the upper peak corresponds to donor regions and lower peak corresponds to acceptor region.



Fig 5. HS dnorm of DAC showing the intensity of selected H-Bond, followed by the fingerprint plots of H-O contacts.

The crystal packing of DAC is also stabilized by both $\pi \cdots \pi$ and C-H $\cdots \pi$ interactions, as showed in Figures 6(a) and 6(b). There is one interaction between dimethoxy rings (represented by Cg1, in red) and one other between the amino rings (represented by Cg2, in blue), with Cg \cdots Cg = 4.289 Å. This $\pi \cdots \pi$ interaction is recognized as two triangular shapes like a bowtie over aromatic rings on HS (Figure 6(c))

and is highlighted blue with $d_e \approx d_i \approx J1.8$ Å in the fingerprint plot (Figure 6(e)). Also, there is an interaction between atoms C15 and H15 and Cg2 [D-H···A = C-H···Cg2; $d_{(D-H)} = 0.930$ Å; $d_{(H...A)} = 3.532$ Å; $d_{(D...A)} = 4.435$ Å; $4_{(D-H...A)} = 164.57^{\circ}$], evidenced by a large red depression over the dimethoxy ring (acceptor region) and a blue convex spot over H15 in the shape index HS (Figure 6(d)). Finally, these interactions are represented by C-H contacts and look like "wings" in the fingerprint plots (Figure 6(f)).



Fig 6. $\pi \cdots \pi$ and C-H $\cdots \pi$ interactions involved in the crystal packing of DAC (a); Evidence of these interactions in the shape index HS (b) and fingerprints plots for C \cdots C and C \cdots H contacts (c).

The solid-state characterization was expanded to DAC in powder form, and the structure determined by single-crystal DRX showed to be stable in ambient conditions; however, it underwent a structural phase transition at about 100 K (see Figure 7). The structural parameters refined by Rietveld Method using synchrotron radiation are shown in Table 1.

From the low temperature measurements, one can see an unexpected phase transition, where the low-temp phase seems to have larger lattice parameters (see most intense peaks shift to higher d values).

The Bragg peaks referring to C2/c structure become broad, suggesting the reduction of its crystalline size

domain.



Fig 7. Calculated (red lines) and experimental (black lines) XRPD patterns of DAC collected with different excitation energies at room temperature and low temperature (100 K).

Spectroscopic characterization

The vibrational spectral analysis is discussed based on the characteristic vibrations of the main absorbing groups of DAC. Detailed vibrational assignments of main IR and Raman modes (theoretical and experimental) are shown in Table 3. For visual analysis, the observed and simulated FTIR and FT-Raman spectra are overlapped, as presented in Figures 8(a) and 8(b). The observed discrepancies are justified because the calculations were made for an isolated molecule in a vacuum, while the experiments were performed using a solid sample.



Fig 8. Overlapped experimental (red) and theoretical (black) IR and Raman spectra of DAC (a) from 0 to 4000 cm^{-1} and zoomed region (b) from 200 to 2000 cm⁻¹.

Table 3. Vibrational assignments, scattering activities and scaled frequencies (cm⁻¹) calculated, with CAM-B3LYP/6-311+ G(d), to $C_{17}H_{17}NO_3$. a) Scale factor:0.958; b) Scale factor:0.955. * indicates the most intense experimental peaks.

	Unscaled IR freq.	IR scattering activities	Raman scattering activities	Scaled IR freq.ª	Exp. IR freq.	Scaled Raman freq. ^b	Exp. Raman freq.
Rigid Rings A-B bending; Amine stretching out off plane	280.36	86.1	1.6	268.6		267.7	255.0
The same as before + torsion of H around C(27) in CH3 of ring B	294.64	83.3	1.1	282.3		281.4	277.6 337.2
In plane stretching ring A; bending O(5) and H around C(27)	574.35	35.6	10.6	550.2	491 508	548.5	395.4 409.6*

	Journa	al Pre-pro	of		525		428.9
					556		490.9 508.3 527.3 560.0
Out off plane and out off phase H stretching in amine	638.8	52.69	3.8	612.0	600	610.1	618.5
In plane stretching ring B	683 81	36.6	2	655 1	615 660	653.0	
	005.01	50.0	2	055.1	687*	055.0	
Out off plane stretching of H of ring A	768.99	52.4	3.5	736.7	719 734* 765	734.4	768.3*
Out off plane stretching of H of ring B	840.9	36.29	1	805.6	811* 820 844* 861	803.1	815.8 856.2
Out off plane stretching of H of the open ring	1038.02	41.7	52.5	994.4	925 980*	991.3	
Almost planar Out off phase stretching of H of the open ring;	1043.13	120.2	219.6	999.3	1007	996.2	978.0
In-plane deformation/breathing mode of ring A and out-off	1062.1	61.13	35.6	1017.5	1023	1014.3	1004.9*
In-plane deformation mode of ring B	1082.62	65.2	2.5	1037.1		1033.9	
Another In-plane deformation/breathing mode of ring A and	1099.54	17.7	120.6	1053.4	1045	1050.1	1044.0
Out off phase vibrations of H(20) and H(8) causing a slight In-	1183.22	54.1	55	1133.5	1081	1130.0	1080.1
plane deformation of ring B Out off phase In-plane vibrations of H in ring A	1194.86	254.19	17	1144.7	1145*	1141.1	1142.8
Breathing mode of ring B caused by in-phase and in-plane vib	1209.2	113	159.4	1158.4	1153*	1154.8	1156.4
Similar Breathing mode of ring B caused by in-phase and in-	1237.49	72.5	188.3	1185.5	1210*	1181.8	
In-phase vib of H in the open ring; slight breathing of ring A	1244.62	383.55	35	1192.3	-	1188.6	1196.1
caused by in-plane H vib and C(16)-C(10) stretching Similar In-phase vib of H in the open ring; slight breathing of	1288 11	80.1	21 64	1234.0	1233	1230 1	
rings A and B Deformation of rings A and B; stretching o C(11)-O(1)	1211 /8	130.2	51 22	1256 /	1255	1252.5	1726 1
connecting CH3 In plane Deformation of rings B; huge displacement of H(8)	1216.05	249.6	201 7	1250.4	1061*	1252.5	1272.0
and alternate stretching of C-O connecting CH3's Similar In plane Deformation of rings B; huge displacement of	1510.05	240.0	291.7	1200.0	1201	1250.0	1275.0
H(3 and H(15) in the open ring	1321.4	119.3	17	1265.9	1275	1261.9	
displacement of H(20) and H(15)	1351.93	146.6	8.7	1295.1		1291.1	
displacement of H(22) and H(18)	1364.19	126.21	218	1306.9	1307*	1302.8	1325.0
In plane Deformation of rings A and B; huge displacement of H(22)	1385.2	23	75.6	1327.0	1325	1322.9	
In plane Deformation of rings A and B; huge displacement of H(13) linked to the open ring	1409.32	43.7	247.7	1350.1	1359 1421 1438	1345.9	1345.9
In plane Deformation of ring B; huge displacements of H(20) and H's linked to C(27) in CH3	1477.72	70.13	230.78	1415.7	1452 1466 1486	1411.2	1362.1
In plane Deformation of ring A; huge displacements of H(32), (38) and (22): C(10)-O(9) stretching	1502.96	13.7	319.6	1439.8		1435.3	1420.9
In plane Deformation of ring B; huge displacements of H(28),	1511.2	21.9	179.9	1447.7	1511*	1443.2	1446.5*
huge displacements of H's linked to $C(23)$ in CH3	1526.84	77.15	16.2	1462.7		1458.1	1466.2
huge displacements of H's linked to C(27) in CH3	1527.66	49.2	10.5	1463.5		1458.9	1488.4
In plane Deformation of ring A; huge displacements of H(32), (18) and (22):	1541.23	48.75	168.2	1476.5	1544	1471.9	1512.0
In plane Deformation of ring B; huge displacements of H(8), (2) and (20), C-O alternate stretching and in phase vib of H's in CH3's	1580.01	532.366	191.5	1513.6	1577* 1599	1508.9	1546.1*
In plane Deformation of ring A; huge displacement of H(38), and in phase vib of H's in NH2	1620.78	105.5	768.8	1552.7	1617*	1547.8	1576.2*
In plane Deformation of rings A and B; huge displacements of H(25) and H(26) in NH2; C(10)-O(9) stretching	1652.29	463.09	986	1582.9	1644*	1577.9	1592.3*
In plane Deformation of rings A and B; huge displacements of H(25) and H(26) in NH2 (opposite to the previous mode);	1656.75	161.9	23.3	1587.2		1582.2	

C(10)-O(9) stretching	Journa	al Pre-pro	of				
In plane Deformation of ring B; huge displacements of H(3) and H(20); as well as H(25) and H(26) in NH2; C(10)-O(9) stretching	1675.45	121.6	4195.8	1605.1		1600.1	1601.1*
Almost the same as previous	1685.24	33.44	378.94	1614.5		1609.4	1615.1
Similar vibration of NH2, without C=O vib; but causing a huge deformation of ring A	1696.04	204.55	407.35	1624.8		1619.7	1626.6
Hugh stretching of C(10)-O(9) and C(12)=C(14) in the open ring , slight deformation of rings A and B	1742.82	279.6	649.9	1669.6	1645	1664.4	1644.2
H breathing mode in CH3, mainly in that of C(27)	3037.96	49.7	82.33	2910.4	2830	2901.3	
H breathing mode in CH3, mainly in that of C(33)	3042.14	61.54	184.31	2914.4	2839 2936	2905.2	
Out-off phase vib of H(29) and H(30) in CH3, that of C(27)	3100.52	34.58	35.4	2970.3	2960	2961.0	
					2971 2987		
Out-off phase vib of H(35) and H(36) in CH3, that of C(33)	3105.97	36.51	65.23	2975.5	3002	2966.2	
					3038 3075		
H's stretching/breathing mode in NH2	3580.13	93.1	383	3429.8	3330	3419.0	
Out-off phase vib of H's in NH2	3732.12	83.2	67.1	3575.4	3548	3564.2	

As Figure 8(a) shows, in the region of 3050 cm^{-1} to 3010 cm^{-1} bands of aromatic CH stretching vibrations usually appear ⁵⁰. These theoretical values calculated in this paper are in the region of 3063 cm^{-1} to 3098 cm^{-1} , while in experimental IR these vibrations are in the region of 3072 cm^{-1} to 3003 cm^{-1} .

The carbonyl group stretching vibrations appear for flavonoid and chalcone derivatives in the spectral region $1660 - 1580 \text{ cm}^{-1}$ as a consequence of the conjugation effect that increases the single bond character of carbonyl and vinyl groups⁵¹. These vibrational modes are observed in the experimental IR spectrum in 1617 cm⁻¹ and 1644 cm⁻¹, respectively, and in 1576.2 cm⁻¹ and 1592.3 cm⁻¹ in the experimental Raman spectrum. This value for a vinyl group is in good agreement with the expected value of $1660 - 1600 \text{ cm}^{-1}$ for this vibrational mode. Additionally, DFT calculations assign the C=O band at 1614 cm^{-1} and the C=C band at 1669 cm^{-1} .

The O-CH3 stretching vibration appears in the wide region between 850 and 1100 cm⁻¹ with an intensity varying from weak to strong⁵². These bands are observed in 1045 cm⁻¹ and 1024 cm⁻¹ in vibrational spectra of ABC; on the other hand, 1037 cm⁻¹ and 1058 cm⁻¹ are the theoretical values for this vibration. The asymmetric stretching of the methoxy group attached to an aromatic ring appears in the range 1310 to 1210 cm⁻¹ ⁵². DFT calculations and experimental IR give the range of 1260 cm⁻¹ to 1234 cm⁻¹ as asymmetric methoxy stretching vibrations.

For the amino group, N-H stretch vibrations occur between 3500 cm⁻¹ and 3300 cm⁻¹, primary amines generate two bands, of which the higher frequency band in the pair is due to asymmetric vibration, while the lower frequency band results from symmetric vibration⁵⁰. In the present study, these stretching modes are assigned at 3575 cm⁻¹ and 3429 cm⁻¹ in IR spectrum and at 3568 cm⁻¹ and 3458 cm⁻¹ for theoretical spectra (Figure 8(a)). The blue shifting of NH₂ symmetric stretching is due to the formation of intramolecular N-H...O hydrogen bonding. The N-H scissoring mode, in primary amines, appears as a medium to strong intensity band between 1640 cm⁻¹ and 1560 cm⁻¹ ⁵⁰, while rocking deformation is expected in the 1090–1060 cm⁻¹ region⁵³ and, finally, the wagging mode is expected in the range 520-720 cm⁻¹ ⁵⁴. Our theoretical values for these vibrational modes are 1605 cm⁻¹, 1017 cm⁻¹ and 612 cm⁻¹, respectively. These values are in good agreement with experimental IR and Raman, as can be seen in Table 3 and Figure 8(b).

The C-N stretch absorption in aromatic amines occurs at 1350 to 1250 cm⁻¹ as a medium to strong intensity band. This absorption occurs at a higher frequency because the resonance enhances the double bond character between the ring and the atom of nitrogen bound to it 50 . This stretching mode appears in IR at 1307-1359 cm⁻¹ and in DFT at 1307-1350 cm⁻¹.

For the methyl group, we analyzed the C–H stretching modes. In sp3 C–H stretch, there are two important bands: 2962 cm⁻¹ for asymmetric stretch, and 2872 cm⁻¹ for symmetric stretching vibration mode ⁵⁰. The features at 2830 - 3075 cm⁻¹ region in the IR spectrum can be assigned to these vibrational modes, while our DFT calculations show these modes around 2975 cm⁻¹ and 2910 cm⁻¹, respectively.

Nonlinear Optical Properties

In this section our theoretical results for the electrical parameters of the DAC crystal are presented. We can see from Table 4 that the value of the average electric dipole is 1.22D and the value of the average linear polarizability is $33.33 \times 10^{-24} esu$. The y-component of the dipole moment gives the greatest contribution for the μ -value, and the diagonal components of the linear polarizability tensor,

which are responsible for the calculation of the mean polarizability (equation (2)), are those with the highest values, highlighting the component α_{zz} , which contributes almost half of the $\langle \alpha \rangle$ -value. The off-diagonal terms are considered in the anisotropy of linear polarizability calculated through equation (3), which have the value $28.78 \times 10^{-24} esu$. Also, in Table 4 the CAM - B3LYP/6 - 311 + G(d) results for the second hyperpolarizability (in 10^{-36} esu) for DAC crystal are presented. As can be noted, the tensor component γ_{zzzz} is much larger than the other \Box -components and participates with more than 65% of $\langle \gamma \rangle$ -value.

Table 4. MP2/6 – 311 + G(d) results for the compounds and average values of the dipole moment (D) and linearpolarizability (in 10^{-24} esu) and CAM – B3LYP/6 – 311 + G(d) results for the second hyperpolarizability (in 10^{-36} esu) for DAC crystal.

μ_x	$\mu_{\mathcal{Y}}$	μ_z	$\langle \mu \rangle$			
0.76	-0.92	-0.22	1.22			
α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}	$\langle \alpha \rangle$
30.17	4.52	23.12	-5.12	9.11	46.70	33.33
γ_{xxxx}	γ_{yyyy}	Yzzzz	Үххуу	γ_{yyzz}	γ_{xxzz}	$\langle \gamma \rangle$
19.73	16.95	281.28	6.69	19.93	28.87	85.79

The linear refractive index for the DAC crystal calculated from equation (7) is n = 1.494, and with this value the Lorentz local field factor is f = 1.4108. From these results and the value of the average second hyperpolarizability, which is 85.79×10^{-36} esu, the third-order electric susceptibility $(\chi^{(3)})$, which is an important parameter for determining the nonlinear optical properties of the crystals and can be measured experimentally by the Z-scan technique, was calculated through equation (8), and we found: $\chi^{(3)} = 13.31 \times 10^{-22} m^2 V^{-2}$.

The DAC molecule can be considered a donor-acceptor-donor (D-A-D) type, where the NH_2 group and the two OCH_3 groups behave like electron donors and the chalcone bridge as an electron acceptor group. As the OMe group is a stronger donor group than NH_2 , the charge transfer occurs from

right to left in the DAC molecule, as shown in Figure 9 (a). The value of the $\chi^{(3)}$ for the DAC is high when compared with other chalcone derivatives studied by the Z-scan technique by D'Silva et al., $(2012)^{55}$; namely, (2E)-1-(4-bromophenyl)-3-[4-methylsulfanyl) phenyl]prop-2-en-1-one (4Br4MSP), (2E)-1-(3-bromophenyl)-3-[4(methylsulfanyl) phenyl]prop-2-en-1-one (3Br4MSP) and (2E)-3[4(methylsulfanyl)phenyl]-1-(4-nitrophenyl)prop-2-en-1-one (4N4MSP). The values of the third-order electric susceptibility (in units of $10^{-22}m^2V^{-2}$) of the chalcone derivatives 4Br4MSP and 3Br4MSP are 2.27 and 1.98 respectively⁵⁵, while the value for DAC is 13.31, which is therefore 5.86 and 6.72 times higher than these values, respectively.

The important fact to emphasize about this increase in $\chi^{(3)}$ for DAC (Figure 9(a)) when compared with the other chalcone derivatives, showed in Figures 9(b) and 9(c), is the stronger donor character of the two *OCH*₃ in comparison with *SCH*₃, both bonded at the benzene ring, as can be seen in Figure 9. Also, the electron donor character of the bromine is weaker than the *NH*₂ group, and the value of $\chi^{(3)}$ increase as stronger is the donor group (or acceptor group).

As can be seen from Figure 9(d), the compound 4N4MSP present the highest value of the thirdorder susceptibility, $\chi^{(3)} = 2.36 \times 10^{-22} m^2 V^{-255}$, when compared with the other two 4-methilsulfanyl chalcone derivatives cited above. In this particular case, the molecule type is a acceptor-acceptor-donor (A-A-D) and the increase in the $\chi^{(3)}$ is attributed to the fact that the charge transfer occurs between the two end molecule groups, donor and acceptor⁵⁵, and the longer the charge transfer axis the greater is the nonlinearity ^{55,56}.



Fig. 9. Four Chalcone derivatives, DAC (a), 4Br4MSP (b), 3Br4MSP (c) and 4N4MSP (d); on the right are shown the values of the real part of the third-order electric susceptibility (in units of 10^{-22} m²V⁻² and the molecule types donor-acceptor-donor (D-A-D) or acceptor-acceptor-donor (A-A-D).

Figures 10(a), 10(b) and 10(c) show, respectively, the average linear polarizability $\langle \alpha(-\omega, \omega) \rangle$ and the average second hyperpolarizabilities, $\langle \gamma(-\omega; \omega, 0, 0) \rangle$ and $\langle \gamma(-2\omega; \omega, \omega, 0) \rangle$, as a function of the applied electric field frequencies. The behavior of the curves in Figures 10(a) and 10(b) is similar, presenting a monotonic increase in the parameters with the increase in the frequencies. However, for value respectively, showing that this second parameter presents a more abrupt increase.



Fig. 10. Dynamic evolution of the calculated values of the linear polarizability (in 10^{-24} esu) and second hyperpolarizability (in 10^{-36} esu) for DAC ((a), (b) and (c)) and with respective values of frequencies.

To enrich our understanding of the NLO optical properties of the DAC isolated molecule we consider the effects of the several solvent media on the electric parameters, both in the presence of static and dynamic external electric field. The average values of electronic dipole moment (μ), average molecular linear polarizability $\langle \alpha \rangle$, first hyperpolarizability parallel to dipole moment $\beta_{\parallel} z(0; 0, 0)$ and the average value of the second hyperpolarizability $\langle \gamma \rangle$, were calculated using Density Functional Theory (DFT) at level *CAM* – *B3LYP* with set basis 6 – 311 + G(d). With this purpose, we have considered the solvent media to be: chloroform ($\varepsilon = 4.71$), dichloromethane ($\varepsilon = 8.93$), acetone ($\varepsilon = 20.49$), ethanol ($\varepsilon = 24.85$), methanol ($\varepsilon = 32.61$), dimethyl sulfoxide ($\varepsilon = 46.70$) and water ($\varepsilon = 78.36$), where ε denotes the static dielectric constant of each solvent medium; the gas-phase ($\varepsilon = 1.00$) results are also presented for comparison.

Table 5 shows the DFT results for the average dipole moment $\langle \mu \rangle$, average linear polarizability $\langle \alpha(0;0) \rangle$, first hyperpolarizability $\beta_{\parallel z}(0;0,0)$ and second hyperpolarizability ($\langle \gamma(0;0,0,0) \rangle$) in

solvent media. As can be noted, the absolute values of all electric parameters increases with the increase

in the solvent dielectric constant value.

Table 5. CAM-B3LYP/6-311+G(d) results for the dynamic linear polarizability (in 10 ⁻²⁴ esu), first static
hyperpolarizability (in 10 ⁻³⁰ esu) and second static hyperpolarizability (in 10 ⁻³⁶ esu) for DAC in several solvent
media

Medium	$\langle \mu \rangle$	$\langle \alpha(0;0) \rangle$	$\beta_{ }z(0;0,0)$	$\langle \gamma(0;0,0,0) \rangle$
Gas-Phase	1.32	36.70	-14.93	92.72
Chloroform	1.64	45.33	-28.92	206.36
Dichloromethane	1.68	47.33	-32.32	239.46
Acetone	1.74	48.84	-34.77	265.09
Ethanol	1.75	49.02	-35.12	268.93
Methanol	1.76	49.27	-35.52	273.31
Dimethylsulfoxide	1.77	49.52	-35.91	277.67
Water	1.78	49.75	-36.28	281.80

In Table 6 for $\lambda = 1064.1 nm$ we present our results for $\alpha(-\omega; \omega)$, $\beta_{\parallel} z(-\omega; \omega, 0)$ which corresponds to the Pockels effect, and $\beta_{\parallel} z(-2\omega; \omega, \omega)$ related with the second harmonic generation (SHG). Also shown in Table 6 are the second hyperpolarizabilities, $\gamma(-\omega; \omega, 0, 0)$ and $\gamma(-2\omega; \omega, \omega, 0)$, which correspond to the dc-Kerr effect and dc-SHG. As can be seen, the variation of the absolute values of the electric parameters does not show a well-defined increase with the increase in of the dielectric constant value of the solvent medium, as observed previously in Table 4.

Table 6. CAM-B3LYP/6-311+G(d) dynamic results for the linear polarizability (in 10^{-24} esu), first static hyperpolarizability (in 10^{-30} esu) and second hyperpolarizability (in 10^{-36} esu) for DAC in several solvent media for λ = 1064.1 nm

Medium	$\alpha(-\omega;\omega)$	$\beta_{\parallel} z(-\omega;\omega,0)$	$\beta_{\parallel} z(-2\omega;\omega,\omega)$	$\gamma(-\omega;\omega,0,0)$	$\gamma(-2\omega;\omega,\omega,0)$
Gas-Phase	37.84	-17.70	-26.26	114.96	197.83
Chloroform	43.04	-30.70	-45.68	225.27	391.25
Dichloromethane	42.93	-32.19	-46.55	241.89	406.40
Acetone	42.38	-32.54	-45.55	248.21	401.39

Ethanol	42.41	-32.73Journal P	1 -45.74 0f	250.30	403.90
Methanol	42.11	-32.48	-44.88	248.72	396.12
Dimethylsulfoxide	42.92	-33.76	-47.60	260.46	424.19
Water	42.16	-32.87	-45.25	253.14	401.17

However, we can note that the greatest values of $\beta_{\parallel} z(-2\omega; \omega, \omega)$; $\beta_{\parallel} z(-\omega; \omega, 0)$; $\gamma(-2\omega; \omega, \omega, 0)$ and $\gamma(-\omega; \omega, 0, 0)$ occur for DMSO (DiMethylSulfoxide), which is the polar solvent with the largest dipole moment value, while the greatest value of $\alpha(-\omega; \omega)$ occurs for Chloroform, which is a weak polar solvent. This effect can be explained by the increasing of the oxygen O1 charge, which acts as an electrons receptor of the benzene ring A, decreasing the electron density and the resonant stability, making it difficult to the electrophilic attack. The charge of the benzene ring A is 0.140e in gas-phase, 0.134e in chloroform and 0.151e in DMSO. The total charge of the benzene ring A-O1 is -0.45e in gas-phase, -0.49e in chloroform and -0.485e in DMSO. More details about transfer charge in gas-phase, chroloform and DMSO can be seen in Table 7.

Table 7: CAM-B3LYP/6-311+G(d) results for the CHELPG atomic charges of DAC in solvent medium

		Charge (e)	
Atom	Gas-phase	Chloroform	DMSO
O3	-0.387067	-0.421206	-0.431907
02	-0.394828	-0.423871	-0.448542
01	-0.592522	-0.627972	-0.636515
C13	0.258014	0.270976	0.26955
C17	0.23231	0.240527	0.22809
H17A	-0.005142	0.005023	0.012514
H17B	0.032645	0.03524	0.03913
H17C	-0.013467	-0.00575	0.003417
C12	-0.16225	-0.169856	-0.175064
H12	0.135582	0.149218	0.157707
C11	-0.295695	-0.302663	-0.301702
H11	0.151407	0.164439	0.167172
C10	0.173544	0.148692	0.153707
C9	-0.008861	0.009886	0.003064
H9	0.104644	0.096941	0.096451
C8	-0.374604	-0.406958	-0.396414
H8	0.128571	0.15106	0.151918
C7	0.650884	0.674342	0.655201
C6	-0.262821	-0.277926	-0.259031

C1	-0.06129	P-0.060135	-0.081129
H1	0.087021	0.092755	0.105589
C2	-0.206889	-0.215003	-0.20794
H2	0.108526	0.118908	0.121684
C3	-0.002218	-0.011454	-0.014603
H3	0.09193	0.102691	0.107382
C14	0.30386	0.30011	0.318667
C16	0.228802	0.221717	0.233387
H16A	-0.009541	0.005093	0.006546
H16B	0.033249	0.038797	0.037413
H16C	-0.008008	0.003884	0.006855
C15	-0.364944	-0.352587	-0.380379
H15	0.197643	0.204054	0.22154
C4	-0.3368	-0.330392	-0.338112
H4	0.139255	0.150348	0.159483
C5	0.583325	0.564597	0.557956
N1	-1.017371	-1.014227	-1.017664
H1A	0.410895	0.423257	0.429805
H1B	0.452213	0.447446	0.444774

Conclusions

Here we have elucidated for the first time the molecular and supramolecular structure of a 3',4'-dimethoxy-2-aminochalcone. Slight rotations on the single bond axes in the propenone core are responsible for deviating the molecule backbone from a perfectly planar structure. An intramolecular hydrogen bond between carbonyl and amine moieties helps stabilize this conformation, while the crystal packing is featured by the formation of cross-linked chains running in opposite directions. Contacts of the type N-H…Omethoxy and C-Hmethyl…Ocarbonyl keep the molecules in contact with these tied chains. We believe that the structural knowledge derived from this study will be useful to understand the biological and physicochemical properties of this chalcone and other related compounds.

The ab-initio calculation studies were performed with the aim of elucidating the non-linear optical properties of a Novel Chalcone Derivative (3',4'-dimethoxy-2-aminochalcone) of the structural formula $C_{17}H_{17}NO_3$. The SM approach was used to simulate the crystalline environment of the DAC crystal, and the third order macroscopic susceptibility value obtained for the DAC crystal was $13.31 \times 10^{-22} m^2 V^{-2}$, higher than the values measured for three chalcone derivatives by the Z-scan technique ⁵⁴. The effects of the solvent media on the molecular properties were considered through the PCM method, where the higher values of $\beta \| z(-2\omega; \omega, \omega); \beta \| z(-\omega; \omega, 0); \gamma(-2\omega, \omega, \omega, 0)$ and $\gamma(-\omega; \omega, 0, 0)$ occurred for the solvent dimethylsulfoxide, which is the polar solvent with the highest dipole moment, while the highest value of $\alpha(-\omega; \omega)$ occurred for chloroform, which is a

weak polar solvent. As a consequence, the DAC crystal exhibits good non-linear optical properties.

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References

- (1) Kateb, B. A.; Hussien, A. A.; Baig, H. M.; Baseer, M. A.; Kulkarni, P. A. Antimicrobial Screening of Novel 4-Hydroxy Chalcones. *W. J. Pharm. Pharm. Sci.* **2016**, *5* (9), 1855–1863.
- (2) Rahman, M. A. Chalcone : A Valuable Insight into the Recent Advances and Potential. *Chem. Sci. J.* **2011**, *2011* (3), CSJ-29.
- (3) Custodio, J. M. F.; Faria, E. C. M.; Sallum, L. O.; Duarte, V. S.; Vaz, W. F.; De Aquino, G. L. B.; Carvalho, P. S.; Napolitano, H. B. The Influence of Methoxy and Ethoxy Groups on Supramolecular Arrangement of Two Methoxy-Chalcones. *J. Braz. Chem. Soc.* **2017**, *28* (11).
- (4) Avupati, V. R.; Rajendra, P.; Yejella, P. CHALCONES : A Mini Review. W. J. *Pharm. Pharm. Sci.* **2014**, *3* (10), 1713–1742.
- (5) Amanaganti, J.; Subhashini, N. Potencial Biological Activity of Chalcones: A Review. *Int. J. Chem. Sci.* **2013**, *11* (3), 1335–1341.
- Wang, Z. Claisen-Schmidt Condensation. Compr. Org. Name React. Reagents 2010, 660–664.
- (7) Dong, F.; Jian, C.; Zhenghao, F.; Kai, G.; Zuliang, L. Synthesis of Chalcones via Claisen – Schmidt Condensation Reaction Catalyzed by Acyclic Acidic Ionic Liquids. *Catal. Commun.* 2008, *9*, 1924–1927.
- (8) Prasad, Y. R.; Rao, A. L.; Rambabu, R. Synthesis and Antimicrobial Activity of Some Chalcone Derivatives. *E-Journal Chem.* **2008**, *5* (3), 461–466.
- (9) Lan, Y.; Chen, Y.; Xu, X.; Qiu, Y.; Liu, S.; Liu, X.; Liu, B. F.; Zhang, G. Synthesis and Biological Evaluation of a Novel Sigma-1 Receptor Antagonist Based on 3,4-Dihydro-2(1H)-Quinolinone Scaffold as a Potential Analgesic. *Eur. J. Med. Chem.* 2014, *79*, 216–230.
- (10) Won, S.-J.; Liu, C.-T.; Tsao, L.-T.; Weng, J.-R.; Ko, H.-H.; Wang, J.-P.; Lin, C.-N. Synthetic Chalcones as Potential Anti-Inflammatory and Cancer Chemopreventive Agents. *Eur. J. Med. Chem.* 2005, *40* (1), 103–112. https://doi.org/10.1016/j.ejmech.2004.09.006.
- (11) Kumar, R.; Mohanakrishnan, D.; Sharma, A.; Kumar, N.; Kalia, K. Reinvestigation of Structure e Activity Relationship of Methoxylated Chalcones as Antimalarials : Synthesis and Evaluation of 2, 4, 5-Trimethoxy Substituted Patterns as Lead Candidates Derived from Abundantly Available Natural b -Asarone. *Eur. J. Med. Chem.* 2010, 45 (11), 5292–5301.
- (12) El Sayed Aly, M. R.; Abd El Razek Fodah, H. H.; Saleh, S. Y. Antiobesity, Antioxidant and Cytotoxicity Activities of Newly Synthesized Chalcone Derivatives and Their Metal Complexes Dedicated to Professor R. R. Schmidt on the Occasion of His 79th Birthday. *Eur. J. Med. Chem.* **2014**, *76*, 517–530.
- (13) Vaz, W.; Custodio, J.; Silveira, R.; Castro, A.; Campos, C.; Anjos, M.; Oliveira, G.; Valverde, C.; Baseia, B.; Napolitano, H. Synthesis, Characterization, and Third-Order Nonlinear Optical Properties of a New Neolignane Analogue. *R. Soc. Chem.* 2016, 6 (79215–79227).

- (14) Sai Kiran, M.; Anand, B.; Siva Sankara Sai, S.; Nageswara Rao, G. Second- and Third-Order Nonlinear Optical Properties of Bis-Chalcone Derivatives. J. Photochem. Photobiol. A Chem. 2014, 290, 38–42.
- (15) Abegão, L. M. G.; Fonseca, R. D.; Santos, F. A.; Souza, G. B.; Barreiros, A. L. B. S.; Barreiros, M. L.; Alencar, M. A. R. C.; Mendonça, C. R.; Silva, D. L.; De Boni, L.; et al. Second- and Third-Order Nonlinear Optical Properties of Unsubstituted and Mono-Substituted Chalcones. *Chem. Phys. Lett.* 2016, 648, 91–96.
- (16) Krawczyk, P.; Pietrzak, M.; Janek, T.; Jędrzejewska, B.; Cysewski, P.
 Spectroscopic and Nonlinear Optical Properties of New Chalcone Fluorescent Probes for Bioimaging Applications: A Theoretical and Experimental Study. J. Mol. Model. 2016, 22 (6), 125.
- (17) Ali, M.; Elzupir, A.; Ibrahem, M.; Suliman, I.; Modwi, A.; H, I.; Ibnaouf, K. Characterization of Optical and Morphological Properties of Chalcones Thin Films for Optoelectronics Application. *Opt. J. Light Electron Opt.* 2017, 145, 529–533.
- Maidur, S.; Jahagirdar, J.; Patil, P.; Chia, T.; Quah, C. Structural Characterizations, Hirshfeld Surface Analyses, and Third-Order Nonlinear Optical Properties of Two Novel Chalcone Derivatives. *Opt. Mater. (Amst).* 2018, 75, 580–594.
- Patil, P.; Maidur, S.; Rao, S.; Dhamaprakash, S. Crystalline Perfection, Third-Order Nonlinear Optical Properties and Optical Limiting Studies of 3,4-Dimethoxy-4'-Methoxychalcone Single Crystal. *Opt. Laser Technol.* 2016, *81*, 70–76.
- (20) Chaudhry, A.; Irfan, A.; Muhammad, S.; Ali-Sehemi, A.; Ahmed, R.; Jingping, Z. Computation Study of Structural, Optoelectronic and Nonlinear Optical Properties of Dynamic Solid-State Chalcone Derivates. *J. Mol. Graph. Model.* 2017, 75, 355–364.
- (21) Shetty, T.; Raghavendra, S.; Dharmaprakash, S. Optical Limiting Studies on Chalcone Doped PMMA Polymer Film. *Mater. Today Proc.* **2016**, *3* (6), 2163–2168.
- (22) Shkir, M.; AlFaify, S.; Arora, M.; Ganesh, V.; Abbas, H.; Yahia, I. S. A First Principles Study of Key Electronic, Optical, Second and Third Order Nonlinear Optical Properties of 3-(4-Chlorophenyl)-1-(Pyridin-3-Yl) Prop-2-En-1-One: A Novel D-pi...π-A Type Chalcone Derivative. *J. Comput. Electron.* **2018**, *17* (1), 9–20.
- (23) AlFaify, S.; Shkir, M.; Arora, M.; Irfan, A.; Algarni, H.; Abbas, H.; Al-Sehemi, A. G. Quantum Chemical Investigation on Molecular Structure, Vibrational, Photophysical and Nonlinear Optical Properties of 1-Threoninium Picrate: An Admirable Contender for Nonlinear Applications. *J. Comput. Electron.* 2018, *17* (4), 1421–1433.
- (24) SADABS; APEX2; SAINT. Bruker AXS Inc. Wisconsin: Madison 2009.
- (25) Sheldrick, G. A Short History of SHELX. *Acta Crystallogr. Sect. A* 2008, 64, 112–122.
- (26) Bruno, I.; Cole, J.; Edginton, P.; Kessler, M.; Macrae, C.; McCabe, P.; Pearson,

J.; Taylor, R. New Software for Searching the Cambridge Structural Database and Visualizing Crystal Structures. *Acta Crystallogr. Sect. B* **2002**, *58*, 389–397.

- (27) Farrugia, L. ORTEP-3 for Windows a Version of ORTEP-III with a Graphical User Interface (GUI). J. Appl. Crystallogr. **1997**, *30*, 565.
- (28) Spackman, M. A.; Jayatilaka, D. Hirshfeld Surface Analysis. *CrystEngComm* **2009**, 19–32.
- (29) Hirshfeld, F. L. Spatial Partitioning of Charge Density. *Isr. J. Chem.* **1977**, *16*, 198–201.
- (30) McKinnon, J.; Spackman, M.; Mitchell, A. Novel Tools for Visualizing and Exploring Intermolecular Interactions in Molecular Crystals. *Acta Crystallogr. Sect. B* **2004**, *60*, 627–668.
- (31) Soudani, S.; Ferretti, V.; Jelsch, C.; Lefebvre, F.; Ben Nasr, C. Crystal Structure, Hirshfeld Surface Analysis, Quantum Mechanical Study and Spectroscopic Studies of Noncentrosymmetric (S)Nicotiniumtrichloridozincate Monohydrate Complex. *Inorg. Chem. Commun.* 2015, *61*, 187–192..
- (32) David, W. I. F.; Shankland, K.; van de Streek, J.; Pidcock, E.; Motherwell, W. D. S.; Cole, J. C. DASH : A Program for Crystal Structure Determination from Powder Diffraction Data. *J. Appl. Crystallogr.* 2006, *39* (6), 910–915.
- (33) Scott, A. P.; Radom, L. Harmonic Vibrational Frequencies: An Evaluation of Hartree–Fock, Møller–Plesset, Quadratic Configuration Interaction, Density Functional Theory, and Semiempirical Scale Factors. J. Phys. Chem. 1996, 100 (41), 16502–16513.
- (34) Barnes, L.; Schindler, B.; Allouche, A.-R.; Simon, D.; Chambert, S.; Oomens, J.; Compagnon, I. Anharmonic Simulations of the Vibrational Spectrum of Sulfated Compounds: Application to the Glycosaminoglycan Fragment Glucosamine 6-Sulfate. *Phys. Chem. Chem. Phys.* **2015**, *17* (39), 25705–25713.
- (35) Fonseca, T. L.; Sabino, J. R.; Castro, M. A.; Georg, H. C. A Theoretical Investigation of Electric Properties of L-Arginine Phosphate Monohydrate Including Environment Polarization Effects. J. Chem. Phys. 2010, 133 (14), 144103.
- (36) Santos, O. L.; Fonseca, T. L.; Sabino, J. R.; Georg, H. C.; Castro, M. A. Polarization Effects on the Electric Properties of Urea and Thiourea Molecules in Solid Phase. J. Chem. Phys. 2015, 143 (23), 234503. https://doi.org/10.1063/1.4937481.
- (37) Santos, O. L.; Sabino, J. R.; Georg, H. C.; Fonseca, T. L.; Castro, M. A. Electric Properties of the 3-Methyl-4-Nitropyridine-1-Oxyde (POM) Molecules in Solid Phase: A Theoretical Study Including Environment Polarization Effect. *Chem. Phys. Lett.* **2017**, *669*, 176–180.
- (38) Valverde, C.; Osorio, A. P. F.; Fonseca, T. L.; Baseia, B. DFT Study of Third-Order Nonlinear Susceptibility of a Chalcone Crystal. *Chem. Phys. Lett.* **2018**.
- (39) KLEINMAN, D. A. Nonlinear Dielectric Polarization in Optical Media. *Phys. Rev.* **1962**, *126*, 1977–1979.
- (40) Senthil, K.; Kalainathan, S.; Kumar, A. R.; Aravindan, P. G. Investigation of Synthesis, Crystal Structure and Third-Order NLO Properties of a New

Stilbazolium Derivative Crystal: A Promising Material for Nonlinear Optical Devices. *RSC Adv.* **2014**, *4* (99), 56112–56127.

- (41) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian 09, Revision A.02. *Gaussian Inc Wallingford CT*. Gaussian, Inc. 2009, p Wallingford CT.
- (42) Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange–Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393* (1–3), 51–57.
- (43) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self □ consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions. J. Chem. Phys. 1980, 72 (1).
- (44) Ramos, R.; da Silva, C.; Guimarães, F.; Martins, F. Polymorphism and Conformerism in Chalcones. *CrystEngComm* **2016**, *18*, 2144–2154.
- (45) Chantrapromma, S.; Ruanwas, P.; Fun, H. (E)-1-(2-Amino-Phen-Yl)-3-(3,4,5-Trimeth-Oxy-Phen-Yl)Prop-2-En-1-One. *Acta Crystallogr. Sect. E* 2011, 67, 2485–2486.
- (46) Attar, S.; O'Brien, Z.; Alhaddad, H.; Golden, M.; Calderón-Urrea, A. Ferrocenyl Chalcones versus Organic Chalcones: A Comparative Study of Their Nematocidal Activity. *Bioorg. Med. Chem.* 2011, 19, 2055–2073.
- (47) Silver, N.; Boykin, D. Substituent Effects on the Carbonyl Stretching Frequency of Chalcones. J. Org. Chem. **1970**, 35 (3), 759–764.
- (48) Opletalová, V.; Harti, J.; Palát Jr, K.; Patel, A. Conformational Analysis of 2-Hydroxy-2',5'-Diazachalcones. J. Pharm. Biomed. Anal. **2000**, 23 (1), 55–59.
- (49) Koziowski, D.; Trouillas, P.; Calliste, C.; Marsal, P.; Lazzaroni, R.; Jean-Luc, D. Density Functional Theory Study of the Conformational, Electronic, and Antioxidant Properties of Natural Chalcones. *J. Phys. Chem. A* 2007, *111* (6), 1138–1145.
- (50) Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Vyvyan, J. A. *Introduction to Spectroscopy*, 5th Editio.; Cengage Learning: Mason, Ohio, 2015.
- (51) de Toledo, T. A.; da Costa, R. C.; Bento, R. R. F.; Al-Maqtari, H. M.; Jamalis, J.;
 Pizani, P. S. Studies on Structural, Optical, Thermal and Vibrational Properties of Thienyl Chalcone Derivative: 1-(4-Nitrophenyl)-3-(2-Thienyl)Prop-2-En-1-One. *J. Mol. Struct.* 2018, 1155, 634–645.
- (52) Panicker, C. Y.; Varghese, H. T.; John, M. A.; Harikumar, B. IR, Raman and Ab-Initio Calcualtions of 2, 6-Dimethoxyphenol. *Orient. J. Chem.* **2008**, *24* (3), 973–976.
- (53) Varsányi, G.; Láng, L. Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives; Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives; Wiley: New York, 1974.
- (54) Özdemir, Ü. Ö.; Güvenç, P.; Şahin, E.; Hamurcu, F. Synthesis, Characterization and Antibacterial Activity of New Sulfonamide Derivatives and Their Nickel(II), Cobalt(II) Complexes. *Inorganica Chim. Acta* **2009**, *362* (8), 2613–2618.
- (55) D'silva, E. D.; Podagatlapalli, G. K.; Venugopal Rao, S.; Dharmaprakash, S. M.

Study on Third-Order Nonlinear Optical Properties of 4-Methylsulfanyl Chalcone Derivatives Using Picosecond Pulses. *Mater. Res. Bull.* **2012**, *47* (11), 3552–3557.

(56) Poornesh, P.; Ravi, K.; Umesh, G.; Hegde, P. K.; Manjunatha, M. G.; Manjunatha, K. B.; Adhikari, A. V. 3,3'-Benzene-1,4-Diylbis[1-(Substituted)Phenylprop-2-En-1-One] Derivatives: A New Class of Materials for Third-Order Nonlinear Optical Applications. *Opt. Commun.* 2010, 283 (7), 1519–

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Highlights

- The new methoxy-aminochalcone presented has deviation from planarity because of rotations in the propenone core;
- An intramolecular H-bonding might help on the molecular stabilization;
- The nonlinear optical properties of this chalcone is higher than others from literature;
- Molecular properties are strongly dependent on the solvent used for calculations;

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