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PII: S0022-2860(20)30364-1

DOI: https://doi.org/10.1016/j.molstruc.2020.128039

Reference: MOLSTR 128039

To appear in: Journal of Molecular Structure

Received Date: 1 February 2020

Revised Date: 8 March 2020

Accepted Date: 8 March 2020

Please cite this article as: M.H. Faizi, F.A.P. Osório, C. Valverde, Synthesis, crystal structure, spectroscopic and nonlinear optical properties of organic salt: A combined experimental and theoretical study, *Journal of Molecular Structure* (2020), doi: https://doi.org/10.1016/j.molstruc.2020.128039.

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# Synthesis, crystal structure, spectroscopic and nonlinear optical properties of organic salt: A combined experimental and theoretical study

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#### Abstract

The 2-methoxy-pyrido[1,2-a]quinoxalin-11-ylium bromide (2MPQYB) crystal was characterized from single crystal X-ray diffraction (XRD) and spectroscopy analysis. The fluorescence spectrum of the compound showed one broad peak at 473 nm. The supramolecular arrangement in solid state was confirmed by 2D-fingerprint plots and Hirshfeld surface analysis. An additional topological analysis from quantum theory of atoms in molecules (QTAIM) highlights the observed halogen bonds on solid state for 2MPQYB. Also the supermolecule (SM) approach was used to simulate the crystalline environment with 246,064 atoms and an *ab-initio* calculation method, which includes the Density Functional Theory (DFT) at CAM-B3LYP/6-311++G(d,p) level, was used to estimate the crystal linear refractive index and the third-order nonlinear susceptibility at the frequency of  $\omega = 0.086 \ a.u.$  ( $\lambda$ =532 nm) and the obtained values were 1.85 and  $\chi^3 = 621.14 \times 10^{-22} m^2/V^2$  respectively. This  $\chi^3$ -value is up to 312.13 times greater than obtained for others organic crystals of the literature, thus indicating that the 2MPQYB can be considered for various applications of NLO materials.

Keywords: UV-visible absorption; Fluorescence spectrum; Hirshfeld surface; linear refractive index; QTAIM

## 1 Introduction

The synthesis of new organic compounds with large nonlinear optical (NLO) properties for potential applications in photonic devices [1,2], as well as in spectroscopy [3,4], frequency modulators [5], and data transmission [6], has been subject of study of several works in the recent years. The organic

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materials present several advantages as compared with inorganic materials, mainly due to the fact that the NLO properties can be controlled by structural modifications or by changing the substituent and the functional groups on the starting reactants.

Among the organic compounds the Quinoxalines are an important class of heterocyclic compounds used as dyes, pharmaceuticals and the moiety is present in number of antibiotics[7]. In the literature only similar tricyclic quinoxaline derivative, pyrido[1,2a]quinoxalin-11-ylium perchorate ([P1]ClO<sub>4</sub>) reported which is formed by Cu(II) mediated cyclization of a simple Schiff base precursor (L1)[8]. Only three other tricyclic heterocycles with similar structure are known (Figure 1) [9–13]. Benzo[e]pyrido[2,1-c][1,2,4]triazin-11-ium salts reported by Goswami et al. are highly fluorescent and shows strong binding with calf thymus DNA [12,13]. Pyrido[1,2-a] quinoxalinium ions reported by Chernavskaya et al. [10] and structurally characterized by Duffy et al. [9] showed antimicrobial activity as well as pH sensitive fluorescence. Except our earlier report [14], none of these syntheses involves halogen.

Ligand oxidation due to metal reduction has been of current interest and recently Reedjik et al reported[15] synthesis of a leuco-verdazyl ring cyclization as a result of Mn(III) reduction. Thus considering the newness of the molecule, potential use of pyrido[1,2-a]quinoxalinium derivatives as fluorescent heterocyclic dyes and recent development of metal mediated cyclization providing new type of heterocyclic compounds. The result presented in this manuscript shows that the reaction can be extended to other moiety and the choice of metal ion or Br<sub>2</sub>/I<sub>2</sub> as oxidizer. Few selected methods reported for structurally close molecule involve multi-step synthetic protocols, which is both labor and chemical intensive [16]. Therefore, synthesis and complete characterization of this special class of quinoxaline (i.e. pyrido [1,2-a]quinoxaline and oxidized salt) is of importance as it may help medicinal and material chemist to develop scaffold/materials based on this core. Considering this challenge, we present herein a facile method to synthesize halogenated product, 2-methoxy-pyrido[1,2-a]quinoxalin-11-ylium bromide.



Figure 1. Molecular structures of (a) pyrido[1,2a]quinoxalin-11-ylium, (b) Benzo[e]pyrido[2,1-c][1,2,4]triazin-11-ium, (c) Pyrido[1,2-a]quinoxaline Phosphate and (d) Pyrido[1,2-a]quinoxalinium ions.

In this work we described the synthesis, crystallization and X-ray characterization of 2-methoxypyrido[1,2-a]quinoxalin-11-ylium bromide (2MPQYB). Hirshfeld surface analysis and the fingerprints plots were used to highlight and quantify the most important interactions in the crystal. The Supermolecule (SM) approach was used to simulate the crystalline environment polarization on a molecule of the 2MPQYB where a bulk with 246,064 atoms was build. Using the density functional theory (DFT) at CAM-B3LYP/ 6-311++G(d,p) level the linear polarizability and the second order hyperpolarizability, as function of the electric field frequency, were calculated.

## 2 Experimental and Computational Procedures

### 2.1 Synthesis and crystallization

#### 2.1.1 Synthesis of 4-Methoxy-N-pyridine-2ylmethylenebenzenamine

Pyridine-2-carbaldehyde (0.43 g, 4.10 mmol) was added dropwise to a methanolic solution (20 mL) of *p*-methoxyaniline (0.50 g, 4.10 mmol). The reaction mixture was stirring for 2 h at room temperature, the product did not precipitate. The solvent was completely removed through high vacuum and a light yellow liquid was obtained. The compound was extracted from reaction mixture by hexane (3 × 10 mL) and evaporated to dryness a light yellow compound was obtained. A dark crystalline compound was obtained from a vacuum desiccator after 2 days. The yield of the product was found (0.50 g, 58%) (Scheme 1). Characterization data for **4-Methoxy-N-pyridine-2ylmethylenebenzenamine**: Melting point 52-53 °C. ESI-MS (M+H<sup>+</sup>): Calcd 213.09; Found 213.09. UV/vis (MeOH):  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>): 341 (15,000) 286 (12,000) 237 (16,000). IR (KBr, cm<sup>-1</sup>): v(HC=N) 1631, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-d<sub>1</sub>)  $\delta$  (ppm) 8.70 (1H,d, *J* = 4.8 Hz), 8.63 (1H, s, HC=N), 8.19 (1H, d, *J* = 8.0 Hz), 7.79 (1H, t, *J* = 7.6 Hz), 7.34 (1H, m) 7.34 ( 2H, m), 6.95 (2H, d, *J* = 8.8 Hz). HRMS (ESI) m/z [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O: 213.1022 found: 213.1029.



#### Scheme 1: Synthetic route of 4-Methoxy-N-pyridine-2ylmethylenebenzenamine

#### 2.1.2 Synthesis of 2-methoxy-pyrido[1,2-a]quinoxalin-11-ylium bromide

Molecular bromine (0.15 g, (49.0  $\mu$ L) 1.00 mmol) was added dropwise to a methanolic solution (10 mL) of 4-Methoxy-N-pyridine-2ylmethylenebenzenamine (0.20 g, 1.00 mmol). The color of the solution was changed immediately from yellow to red with highly intense blue fluorescence and a yellow precipitate was formed within a minute. The reaction mixture was continued stirring for another 2 h. The solvent was concentrated to 5 mL, a yellow powder was obtained and was washed with acetone. Fine needle- like yellow crystals were formed in 48 h by slow evaporation from a methanolic solution. The crystals were collected, washed with diethyl ether and dried over silica gel in vacuum desiccator. Yield: (0.14 g, 52%) (Scheme 2).



Scheme 2: Synthetic route of 2MPQYB

Characterization data for 2-methoxy-pyrido[1,2-a]quinoxalin-11-ylium bromide (2MPQYB): Melting point 285-287 °C.  $\Lambda_{\rm M}$  (MeOH): 119 S cm<sup>2</sup> mol<sup>-1</sup>. HRMS (ESI) m/z [M]+ calcd for C<sub>13</sub>H<sub>11</sub>N<sub>2</sub>O: 211.0871 found: 211.086 (Figure 2(a)). UV/vis (MeOH):  $\lambda_{\rm max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>):272 (22,000), 243 (14,000), 305 (sh), 401(13,000). IR (KBr, cm<sup>-1</sup>): v(C=N)1615. Fluorescence (MeOH) : $\lambda_{\rm ex}$ , 400 nm;  $\lambda_{\rm em}$ 473 nm. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm) 10.50 (1H, d, *J* = 6.8 Hz), 9.71 (1H, s), 8.95 (1H, d, *J* = 8.0 Hz), 8.90 (1H, t, *J* = 8.4 Hz), 8.57 (1H, t, *J* = 6.8 Hz) 8.51 (1H, s), 8.57 (1H, d, *J* = 9.2 Hz), 7.81 (H, d, *J* = 9.2 Hz), 4.12 (3H, s) (Figura 2(b)). The <sup>1</sup>H <sup>1</sup>H-COSY NMR spectrum of the compound are shown Figure 3.



Figure 2 (a) HRMS (ESI) mass spectrum and (b) <sup>1</sup>H NMR spectrum with numbering scheme of 2-methoxy-pyrido[1,2-a]quinoxalin-11-ylium bromide (only the aromatic region is shown for clarity).



Figure 3 The <sup>1</sup>H <sup>1</sup>H-COSY NMR spectrum of 2-methoxy-pyrido[1,2-*a*]quinoxalin-11-ylium bromide in DMSO-d<sub>6</sub> at 400 MHz (only the aromatic region is shown for clarity).

#### 2.2 X-ray Data Collection, Structure Solution and Refinement

Crystals of the compound 2MPQYB obtained during synthesis were used for X-ray analysis. The crystals were mounted on glass fiber. Absorption corrections were done using SADABS only as either kinds of absorption did not help. After the initial solution and refinement with SHELXL, the final refinements were performed on WinGX environment using SHELX97. Selected crystallographic data

have been summarized in Table 1. The crystals of both compounds were mounted on glass fiber. All geometric and intensity data for the crystals were collected at room temperature using a Bruker SMART APEX CCD diffractometer equipped with a fine focus 1.75 kW sealed tube Mo K $\alpha$  ( $\lambda = 0.71073$  Å) X-ray source, with increasing  $\omega$  (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition and the SAINT software for data extraction. Structures were solved and refined using SHELX97. All non-hydrogen atoms were refined isotropically.

Chemical formula	$C_{13}H_{11}N_2O \cdot Br$
M <sub>r</sub>	291.15
Crystal system, space group	Monoclinic, P2 <sub>1</sub> /n
Temperature (K)	296
a, b, c (Å)	7.7851 (8), 9.9092 (10), 15.3579 (16)
β (°)	94.872 (7)
V (Å <sup>3</sup> )	1180.5 (2)
Z	4
Radiation type	Μο Κα
μ (mm <sup>-1</sup> )	3.47
Crystal size (mm)	$0.20\times0.15\times0.10$
Diffractometer	CCD area detector
Absorption correction	multi-scan
T <sub>min</sub> , T <sub>max</sub>	0.544, 0.723
No. of measured, independent and	11277, 2070, 1479
observed $[I > 2\sigma(I)]$ reflections	
R <sub>int</sub>	0.073
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.594
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.059, 0.164, 1.01
No. of reflections	2070
No. of parameters	154
H-atom treatment	H-atom parameters constrained

Table 1 Crystallographic data and structure refinement of 2MPQYB

$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} \ (e \ \text{\AA}^{-3})$	1.19, -0.67
CCDC reference: 1546353	

#### 2.3 Hirshfeld Surface

In order to evaluate and analyze with details the molecular packing and supramolecular arrangement of 2MPQYB the Hirshfeld surface (HS) analyses and the 2D fingerprint plots were performed. The Hirshfeld surfaces [17] and the associated 2D fingerprint plots [18] were calculated using Crystal Explorer 17.5. Hirshfeld surface is a spatial map, constructed by partitioning space into specific regions where the electron distribution of a sum of spherical atoms for the molecule dominates the corresponding sum over the crystal. Hirshfeld defined a weighting function w(r) [19] given by the ratio between the spherical mean of the all atoms in a molecule by the spherical mean of the all atoms in the crystal. The weighting function w(r) similarly can be defined by,

$$w(r) = \frac{\sum_{Amolecule} \rho_A(r)}{\sum_{Acrystal} \rho_A(r)},$$
(1)

where the sums of the spherically-averaged atomic electron density centred on nucleus A ( $\rho_A(r)$ ) are performed in the molecule (numerator) and in the crystal (denominator). The identification of the regions of particular importance to intermolecular interactions is obtained by mapping normalized contact distance ( $d_{norm}$ ), defined by,

$$d_{norm} = \frac{d_i - r_i^{vdW}}{r_i^{vdW}} + \frac{d_e - r_e^{vdW}}{r_e^{vdW}},\tag{2}$$

where  $r_i^{vdW}$  and  $r_e^{vdW}$  are the van der Waals radii of the atoms, and  $d_i$  and  $d_e$  are the distances from the point to the nearest atom off and within the surface respectively. The donor and receptor regions of molecular interactions are visualized in the normalized HS with a color scale to define the intensity of the interactions.

#### 2.4 UV-visible and fluorescence spectra of 2MPQYB.

The UV-visible absorption of 2MPQYB was recorded in the wavelength range of 200 nm to 700 nm using the commercial spectrophotometer (UV2450, Schimadzu, Japan). The emission fluorescence spectra were recorder in the visible region of 400nm to 600nm, with a highest intensity peak in the blue region. Fluorescence spectra were measured on fluorimeter (Fluorolog 3-21, HoribaJobin-Yvon, USA).

#### 2.5 Computational procedures

The crystalline environment polarization on a molecule of the 2MPQYB is simulated by the Supermolecule (SM) approach, where a bulk with 8,788 unit cell each with four asymmetric units totalizing 246,064 atoms was build, Figure 4 illustrates the bulk with one explicit molecule of 2MPQYB (highlighted in green) in the center.



Figure 4: Schematic representation of the 2MPQYB bulk.

The SM approach considers atoms around the 2MPQYB isolated molecule as punctual charges. The iterative process of the supermolecule approach (SM) is taken in several steps: initially we determine the electrical charge of each atom of the asymmetric unit, using the Chelpg method, which is performed by adjusting the molecular electrostatic potential. The partial atomic electric charges of each atom of the isolated molecule are then replaced at each atom of the bulk. The SM iterative approach was calculated using the density functional theory (DFT) with the functional CAM-B3LYP and the 6-311++G(d,p) basis set. The SM process finish with the convergence of the total dipole moment [20–29] given by the

expression:  $\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}}$ . The obtained  $\mu$ -value after six calculation steps was 17.12D (see Figure 5). The efficiency of the SM approach to simulate the macroscopic third-order nonlinear optical (NLO) properties of the organic crystals was well established in several recent works which the theoretical results are found be near of the experimental results [29–31].



Figure 5. Dipole moment (D) as function of the iteration steps.

In the present work the third-order nonlinear susceptibility  $(\chi^{(3)})$  of the 2MPQYB crystal we use the following expression,

$$\chi^{(3)}(-\omega;\omega,\omega,-\omega) = \frac{N}{\epsilon_o V_{uc}} \left(\frac{(n(\omega)^2 + 2)}{3}\right)^4 \langle \gamma(-\omega;\omega,\omega,-\omega) \rangle, \tag{3}$$

where  $\epsilon_o$  is the vacuum permittivity,  $V_{uc}$  is unit cell volume, and N is the number of molecules in the unit cell and  $\langle \gamma(-\omega; \omega, \omega, -\omega) \rangle$  is the average second hyperpolarizability associated to nonlinear optical process of the intensity dependent refractive index (IDRI) that was calculated through the relation for small frequencies [32]  $\langle \gamma(-\omega; \omega, \omega, -\omega) \rangle \approx 2 \langle \gamma(-\omega; \omega, 0, 0) \rangle - \langle \gamma(0; 0, 0, 0) \rangle$  and the average second hyperpolarizability is given by,

$$\langle \gamma \rangle = \frac{1}{15} \sum_{i,j=x,y,z} (\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji}).$$
(4)

The refractive index  $n(\omega)$  values were determined through the Clausius-Mossotti relation given by,

$$\frac{n(\omega)^2 - 1}{n(\omega)^2 + 2} = \frac{4\pi}{3 V_{uc}} \langle \alpha(-\omega; \omega) \rangle,$$
(5)

and the dynamics average linear polarizability ( $\langle \alpha(-\omega; \omega) \rangle$ ) was calculated through the expression,

$$\langle \alpha(-\omega;\omega)\rangle = \frac{1}{3} \sum_{i=x,y,z} \alpha_{ii} (-\omega;\omega).$$
(6)

All the numerical calculations were performed at the DFT/CAM-B3LYP/ 6-311++G(d,p) level via Gaussian-09 [33] software package and the output file are converted by the electronic units (esu).

## 3 Results and discussions

#### 3.1 Crystal Structure of 2MPQYB

The title organic salt,  $C_{13}H_{11}N_2O^+$  Br<sup>-</sup> (2MPQYB) was synthesized by the reaction of the pyridine derivative Schiff base (4-Methoxy-phenyl)-pyridin-2-ylmethylene-amine) with molecular bromine. The asymmetric unit contains a 2-methoxy-pyrido[1,2-a]quinoxalin-11-ylium cation, with a protonated pyridine moiety and a bromide anion. The asymmetric unit of the title compound contains a discrete 2-methoxy-pyrido[1,2-a]quinoxalin-11-ylium cation with a protonated pyridine moiety, and a bromide counter-anion (Figure 6). The cation is non-planar compared to the previously reported structures [14,34]. The mean plane of the pyridine ring forms a dihedral angle of 24.2 (4)° with the benzene ring and 14.6 (4)° with the pyrazine ring of the fused system. The dihedral angle between the pyrazine and the benzene ring is 11.5 (4)° shorting the C10—N3 distance of 1.367 (9)Å, compared to the usual aromatic C—N<sub>amine</sub> single bond distance of 1.43 (3) Å. This fact might be due to the electron withdrawing effect of the positively charged pyridine N atom, and the ortho-substituted bromine atom

which decreases the C—N<sub>amine</sub> bond order. Other C—C and C—N bond distances are well within the limits expected for aromatic rings [8]. The bond distances, angles and dihedral angles of compound 2MPQYB are provided in Table S1 (supplementary file). A view of the packing of the compound is given Figure 7. Present also in the cations are intramolecular C13—H13…Br1, C10—H10…Br1 and C3—H3…Br1 interactions 3.529 (6), 3.743 (7), 3.719 (6) Å, respectively (Figure 8, Table 2)



Figure 6. The molecular structure of the title compound, with the atom labeling and displacement ellipsoids drawn at the 40% probability level.



Figure 7. A view of the 2MPQYB packing



Figure 8. A view of the hydrogen-bonded trimer of the title compound. Dashed lines indicate hydrogen bonds.

D—H···A	<i>D</i> —Н	H···A	$D \cdots A$	D—H···A
C13—H13····Br1 <sup>i</sup>	0.93	2.64	3.529 (6)	161.1
C12—H12…O1 <sup>ii</sup>	0.93	2.56	3.445 (7)	158.0
C3—H3····Br1 <sup>iii</sup>	0.93	2.84	3.719 (6)	158.3
C8—H8····Br1 <sup>iv</sup>	0.93	2.91	3.770 (7)	153.7
C10—H10····Br1 <sup>iv</sup>	0.93	2.88	3.743 (7)	155.1

Table 2. Hydrogen-bond geometry (Å, °)

Symmetry codes: (i) -x+3/2, y+1/2, -z+3/2; (ii) x-1/2, -y+3/2, z+1/2; (iii) -x+2, -y+1, -z+1; (iv) -x+3/2, y-1/2, -z+3/2.

#### 3.2 QTAIM Analysis

An additional topological analysis was performed using the QTAIM methodology [35–37] at the theoretical level DFT/B3LYP/6-311+G(d) [38] coupled in the Gaussian09 package and by Multiwfn software [39]. According to the concepts of quantum chemistry the observable properties are present in the electron density  $\rho(r)$  and energy density [40,41]. The figure 9 shows the existence of bond critical point (BCP) for 2MPQYB compound interactions.



Figure 9. Representation of bond critical points (BCP) for 2MPQYB indicating the bond paths analyzed in Table 3.

The observables of each BCP can be seen in Table 3 where  $[\rho(r)]$  electron density,  $[\nabla^2 \rho(r)]$  is the Laplacian of electron density; V(r) is the potential energy density; G(r) and H(r) are the Lagrangian kinetic energy and electronic energy density respectively, which was obtained through the equation H(r) = G(r) + V(r). For hydrogen bonds  $\nabla^2 \rho(r)$  is positive and  $\rho(r)$  is small and the interaction character can be measured by the indicators: (1)  $\nabla^2 \rho(r) < 0$  and H(r) < 0; strong interactions with covalent character, (2)  $\nabla^2 \rho(r) > 0$  and H(r) < 0; medium strength and (3)  $\nabla^2 \rho(r) > 0$  and H(r) > 0; weak interactions with electrostatic character [37,42].

BCP	$\rho(r_{bcp})$	$\nabla^2 \rho(r_{bcp})$	$V(r_{bcp})$	$G(r_{bcp})$	$H(r_{bcp})$	Interactions
1	0.0182	0.0511	-0.0103	0.0115	0.0012	C13—H13…Br1
2	0.0094	0.0330	-0.0059	0.0071	0.0012	C12—H12…O1
3	0.0121	0.0348	-0.0060	0.0073	0.0014	C3—H3…Br1
4	0.0112	0.0315	-0.0054	0.0067	0.0012	C8—H8…Br1
5	0.0117	0.0334	-0.0057	0.0071	0.0013	C10—H10…Br1

Table 3. Topological analysis performed via QTAIM for 2MPQYB, all data are in a.u..

The electrostatic hydrogen bonds are confirmed by the small values of  $\rho(r)$  and the positive values H(r). As the Laplacian of electron density is positive  $\nabla^2 \rho(r) > 0$ , the electron density is less than 0.10 a.u. ( $\rho(r) < 0.10$  a.u.) and electronic energy density is positive (H(r) > 0) all interactions in Table 3 are closed-shell interactions.

#### 3.3 Hirshfeld surfaces and 2D fingerprints

The Hirshfeld surface (HS) and the associated 2D-fingerprint plots were calculated using Crystal Explorer software. The intercontact are highlighted by conventional mapping  $d_{Norm}$ ,  $d_e$ ,  $d_i$  and the 2D-fingerprint plots. By this way it was possible verified the set of present interactions, but also the relative area of the surface corresponding to each interaction. The red and white spots at  $d_{Norm}$  HS (Figure 10) highlight shorter contacts, the white, represent contacts around the van der Waals separation and the red represent contacts smaller than the sum of van der Waals radii. The red region indicate hydrogen bonds (Figure 10).



Figure 10. Hirshfield surface  $d_{Norm}$  (isovalue = 0.5) highlighting the classical hydrogen interactions.

The 2MPQYB fingerprint plot (Figure 11) indicates that C····H type interactions, which are shaped like a pair of sharp-tipped wings, have 14.4% of Hirshfeld's total surface. Other relevant contributions related to 2MPQYB intermolecular interactions are: H···O 5.3%, N····H 6.6%, Br····H 25.4%, C···C 7% and H····H 36.6%.



Figure 11. Fingerprint plotting, exposing key interactions.

The C···H contacts of the compound indicate a non-classical interaction that makes an important contribution to the stability of the crystalline package.

#### 3.4 UV-VIS spectral analysis

The UV-VIS absorption spectrum from 200nm up to 700nm is shown in the Figure 12 (a), as can be seen the absorption region cover the UV-range of 200nm  $< \lambda < 401$ nm, also a good optical transmission region can be noted between 401nm and 700nm. This fact show that 2MPQYB crystal can be used for NLO device fabrications.



Figure 12. (a) UV-VIS absorption and (b) UV-VIS and Fluorescence of 2MPQYB

The emission fluorescence spectra showed in Figure 12(b) covers the visible electromagnetic range from 420nm to 600nm, with the highest emission intensity in the blue region (473nm). Therefore the difference between the excitation and emission peaks (Stockes shift) is of 73nm.

#### 3.5 NLO properties of 2MPQYB crystal

Table S2 (supplementary file) shows the results for the electric dipole moment for the 2MPQYB, for both isolated and embedded molecule. As can be seen the polarization effect of the crystalline environment on the total dipole moment is significant for the 2MPQYB, the  $\mu$ -value for the embedded molecule is 17.19D, presenting an increase of 25.75% in comparison with the isolated molecule. The  $\mu_x$ component presented the greatest increase due to the crystalline environment polarization.

The dispersion relations of the average linear polarizability ( $\langle \alpha(-\omega; \omega) \rangle$ ) and of the linear refractive index ( $n(\omega)$ ) of 2MPQYB crystal in the electric field frequency range of  $0 < \omega < 0.10 \ a. u$ . are shown in Figure 13. As can be seen from Figure 13 the values of the both functions,  $\langle \alpha(-\omega; \omega) \rangle$  and  $n(\omega)$ ,

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increases monotonically with the frequency increasing, from  $28.1 \times 10^{-24} esu$  to  $35.5 \times 10^{-24} esu$  and from 1.63 to 1.93 respectively.



Figure 13. (a) Dynamic linear polarizability (in  $10^{-24}esu$ ) and the (b) linear refractive index as function of the electric field frequency for 2MPQYB crystal.

Figure 14(a) shows the hyperpolarizabilities  $\langle \gamma(-\omega; \omega, 0, 0) \rangle$  and  $\langle \gamma(-\omega; \omega, \omega, -\omega) \rangle$  as function of the frequency. Both functions start from the static value  $\langle \gamma(0; 0, 0, 0) \rangle = 35.88 \times 10^{-36} esu$ , and at the frequency of  $\omega = 0.086$  a.u. the value of the IDRI second hyperpolarizability ( $\langle \gamma(-\omega; \omega, \omega, -\omega) \rangle$ ) is  $122.71 \times 10^{-36} esu$ , that is 54.8% greater than the dc-Kerr second hyperpolarizability ( $\langle \gamma(-\omega; \omega, 0, 0) \rangle$ ).



Figure 14. (a) Average second hyperpolarizabilities (in  $10^{-36}esu$ ) and (b) third-order nonlinear susceptibility (in  $10^{-22}m^2/V^2$ ) as function of the electric field frequency for 2MPQYB crystal.

The third-order nonlinear susceptibility values as function of the frequency are shown in Figure 14(b). The  $\chi^3$ -values goes from the static value of  $181.61 \times 10^{-22} m^2/V^2$  to  $1327.58 \times 10^{-22} m^2/V^2$  at  $\omega = 0.10 \ a. u.$ , that is 6.3 times greater than static value. At  $\omega = 0.086 \ a. u.$  ( $\lambda = 532$ nm)  $\chi^3 = 621.14 \times 10^{-22} m^2/V^2$ , this value is 3.4 times greater the  $\chi^3$  static value. All values of the dipole moment, linear polarizability, refractive index, and third-order susceptibility are in the Tables S2-S7 (supplementary file).

Table 4 shows experimental results for the third-order susceptibility obtained for some organic crystals. As can be noted the  $\chi^3$ -value for 2MPQYB is greater than the values presented in the Table 4. Particularly the present result for 2MPQYB is 2.24 times the experimental value obtained for 3MPNP [43] and 312.13 times larger than the  $\chi^3$ -value for (2E)-1-(3-bromophenyl)-3-[4 (methylsulfanyl) phenyl]prop-2-en-1-one crystal [44], therefore the nonlinear optical properties of 2MPQYB are significant and can be explored for potential use in NLO devices.

Also Table 4 shows results for the refractive index of some organic materials and for 2MPQYB crystal at frequency  $\omega = 0.086 \ a. u.$  ( $\lambda$ =532nm), which is the frequency where the Z-scan experiment are frequently performed to measure the third-order nonlinear susceptibility.

	$n(\omega))$	$\chi^{(3)}(-\omega;\omega,\omega,-\omega)$
2MPQYB (this work)	1.851	621.137
(2E)-3-(3-methylphenyl)-1-(4-nitrophenyl)prop-2-en-1-one 3MPNP [43]	1.418	277.100
(2E)-3-(3-methylphenyl)-1-(4-nitrophenyl)prop-2-en-1-one [29]	2.002	176.400
4,6-dichloro-2-(methylsulfonyl)pyrimidine[45]	1.613	56.740
(E)-3-(2-bromophenyl)-1-(2-((phenylsulfonyl)amine)-phenyl)prop-2-en-1-one [46]	1.680	25.700
1-(5-chlorothiophen-2-yl)-3-(2,3-dimethoxyphenyl)prop-2-en-1-one [43,47]	1.594	23.830
1-(5-chlorothiophen-2-yl)-3-(2,3-dichlorophenyl)prop-2-en-1-one [48]	-	16.210
2-(4-methylphenoxy)-N0-[(1E)-(4-nitrophenyl)methylene]acetohydrazide [49]	-	10.240
1-(4-aminophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one [50]	-	8.700
(2E)-3 [4 (methylsulfanyl)phenyl]-1-(4-nitrophenyl)prop-2-en-1-one [44]	1.363	2.370
(2E)-1-(4-bromophenyl)-3-[4-methylsulfanyl) phenyl]prop-2-en-1-one [44]	1.365	2.300
(2E)-1-(3-bromophenyl)-3-[4 (methylsulfanyl) phenyl]prop-2-en-1-one [44]	1.360	1.990

Table 4. Linear refractive index and third-order nonlinear susceptibility  $(10^{-22}m^2/V^2)$  results for some organic materials and for 2MPQYB at wavelength of 532nm.

## 4 Conclusion

A new organic crystal 2-methoxy-pyrido[1,2-a]quinoxalin-11-ylium bromide (2MPQYB) was synthesized by a slow evaporation technique. Single crystal X-ray diffraction analysis confirms that the 2MPQYB crystallizes in the P2<sub>1</sub>/n centrosymmetric monoclinic space group. The presence of carbon and proton is confirmed by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral analyzes. In addition, fluorescence spectra were obtained and shown a Stokes shift of 73nm. The crystalline environment was simulated using the SM approach at DFT/CAM-B3LYP/6-311++G(d, p) level and the total dipole moment ( $\mu$ ), the average  $(\langle \alpha(-\omega;\omega) \rangle)$ linear polarizability and the IDRI average second hyperpolarizability  $(\langle \gamma(-\omega; \omega, \omega, -\omega) \rangle)$ , the linear refractive index (n ( $\omega$ )) and the third order macroscopic susceptibility  $(\chi^{(3)}(-\omega;\omega,\omega,-\omega))$  of the 2MPQYB structure were calculated. The typical value of  $\chi^{(3)}$  reported in the literature is of the order of  $10^{-22} (m/V)^2$ [51]. The 2MPQYB crystal presented a third order macroscopic susceptibility ( $\chi^3 = 621.14 \times 10^{-22} m^2/V^2$ ) at  $\omega = 0.086 a.u.$  ( $\lambda = 532$ nm) higher than some experimental results founded in the literature (Table 4). The theoretical results obtained for the  $\chi$ value for the 2MPQYB crystal is between 2.24 and 312.13 times the reported experimental results for some organic crystals that are presented in the Table 4. Therefore, 2MPQYB crystal is a promising material for use in nonlinear optical device.

#### References

- L. Lu, Z. Liang, L. Wu, Y. Chen, Y. Song, S.C. Dhanabalan, J.S. Ponraj, B. Dong, Y. Xiang, Few-layer Bismuthene: Sonochemical Exfoliation, Nonlinear Optics and Applications for Ultrafast Photonics with Enhanced Stability, 1700221 (2017) 1–10. https://doi.org/10.1002/lpor.201700221.
- R. Salvi, C. Cerqueira-coutinho, E. Ricci-junior, N. Santos, S.R. Pinto, E.S. Bernardes, P. Lopes, B. De Araujo, R. Santos-oliveira, R. Salvi, C. Cerqueira-coutinho, E. Ricci-junior, N. Santos, S.R. Pinto, E.S. Bernardes, P. Lopes, Diagnosing lung cancer using etoposide microparticles labeled with Tc, 1401 (2017). https://doi.org/10.1080/21691401.2017.1307848.
- [3] M. Luo, F. Liang, Y. Song, D. Zhao, F. Xu, N. Ye, Z. Lin, M 2 B 10 O 14 F 6 (M = Ca, Sr): Two Noncentrosymmetric Alkaline Earth Fluorooxoborates as Promising Next-Generation Deep-Ultraviolet Nonlinear Optical Materials, J. Am. Chem. Soc. 140 (2018) 3884–3887. https://doi.org/10.1021/jacs.8b01263.
- [4] H. Zhao, S. Han, R. Hui, Nonlinear Optical Spectroscopy of Two-Dimensional Materials Qiannan Cui, (2017).
- [5] G. Shi, Y. Wang, F. Zhang, B. Zhang, Z. Yang, X. Hou, Finding the Next Deep-Ultraviolet Nonlinear Optical Material:, (2017) 8–11. https://doi.org/10.1021/jacs.7b05943.
- [6] A.N. Castro, L.R. Almeida, M.M. Anjos, G.R. Oliveira, H.B. Napolitano, C. Valverde, B. Baseia, Theoretical study on the third-order nonlinear optical properties and structural characterization of 3-Acetyl-6-Bromocoumarin, Chem. Phys. Lett. 653 (2016) 122–130. https://doi.org/10.1016/j.cplett.2016.04.070.
- [7] J.A. Pereira, A.M. Pessoa, M.N.D.S. Cordeiro, R. Fernandes, C. Prudêncio, J.P. Noronha, M. Vieira, Quinoxaline, its derivatives and applications: A State of the Art review, Eur. J. Med. Chem. 97 (2015) 664–672. https://doi.org/10.1016/j.ejmech.2014.06.058.
- [8] R.R. Koner, M. Ray, Cu II -Mediated Synthesis of a New Fluorescent Pyrido[1,2- a ]quinoxalin-11-ium Derivative †, Inorg. Chem. 47 (2008) 9122–9124. https://doi.org/10.1021/ic8008464.
- [9] J.I.L. and H.-Y.C. Kevin J. Duffy, R. Curtis Haltiwanger, Alan J. Freyer, Florence Li, Pyrido[1,2a]quinoxalines: synthesis, crystal structure determination and pH-dependent fluorescenceElectronic supplementary information (ESI) available: NMR data of compounds 3a– k and views of the crystal structures of 3g, 3i and 3k. See http://www.rsc.or, J. Chem. Soc. Perkin Trans. 2. (2002) 181–185. https://doi.org/10.1039/b102755g.
- [10] L.N. Chernavskaya, N. V. Kholodova, S.G. Blagorodov, N.A. Dmitrieva, Synthesis and antimicrobial activity of pyrido[1,2-a]quinoxalinium perchlorates, Pharm. Chem. J. 18 (1984) 413–416. https://doi.org/10.1007/BF00776797.
- [11] S. Goswami, A.K. Adak, A One-pot Synthesis of Cyclic Pyrido[1,2- a ]quinoxaline Phosphate, a New Molecule of Biological Importance from a Quinoxaline Derivative of Sugar, Chem. Lett. 32

(2003) 678-679. https://doi.org/10.1246/cl.2003.678.

- [12] M. Sinan, K. Ghosh, S. Goswami, One-Pot Synthesis of Linearly Fused N-Heterocyles from Their Angular Analogues and Studies of Their Redox and Electrochromic Properties, J. Org. Chem. 75 (2010) 2065–2068. https://doi.org/10.1021/jo902432w.
- [13] M. Sinan, M. Panda, A. Ghosh, K. Dhara, P.E. Fanwick, D.J. Chattopadhyay, S. Goswami, Mild Synthesis of a Family of Planar Triazinium Cations via Proton-Assisted Cyclization of Pyridyl Containing Azo Compounds and Studies on DNA Intercalation, J. Am. Chem. Soc. 130 (2008) 5185–5193. https://doi.org/10.1021/ja710211u.
- [14] M.S.H. Faizi, M.J. Alam, A. Haque, S. Ahmad, M. Shahid, M. Ahmad, Experimental and theoretical characterization of organic salt: 2-((4-bromophenyl)amino) pyrido[1,2- a ] quinoxalin-11-ium bromide monohydrate synthesized via oxidative cyclization, J. Mol. Struct. 1156 (2018) 457–464. https://doi.org/10.1016/j.molstruc.2017.12.014.
- [15] J. Tang, S. Nayak, J.S. Costa, A. Robertazzi, R. Pievo, I. Mutikainen, O. Roubeau, S.J. Teat, P. Gamez, J. Reedijk, Manganese( <scp>iii</scp> )-mediated cyclodimerization of a hydrazinyl derivative generating an unprecedented 1,2,3,5,6-substituted leuco-verdazyl ring, Dalt. Trans. 39 (2010) 1361–1365. https://doi.org/10.1039/B917410A.
- [16] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, Completion and refinement of crystal structures with SIR 92, J. Appl. Crystallogr. 26 (1993) 343–350. https://doi.org/10.1107/S0021889892010331.
- [17] M.A. Spackman, D. Jayatilaka, Hirshfeld surface analysis, CrystEngComm. 11 (2009) 19–32. https://doi.org/10.1039/B818330A.
- [18] M.A. Spackman, J.J. McKinnon, Fingerprinting intermolecular interactions in molecular crystals, CrystEngComm. 4 (2002) 378–392. https://doi.org/10.1039/B203191B.
- [19] J.J. McKinnon, A.S. Mitchell, M.A. Spackman, Hirshfeld Surfaces: A New Tool for Visualising and Exploring Molecular Crystals, Chem. – A Eur. J. 4 (1998) 2136–2141. https://doi.org/10.1002/(SICI)1521-3765(19981102)4:11<2136::AID-CHEM2136>3.0.CO;2-G.
- [20] C.J.S. Ferreira, C. Valverde, B. Baseia, Atom-field interaction in optical cavities: Calibration of the atomic velocities to obtain a list of field states with preselected properties, Int. J. Mod. Phys. B. 32 (2018) 1850222. https://doi.org/10.1142/S0217979218502223.
- [21] W. Vaz, J. Custodio, R. Silveira, A. Castro, C. Campos, M. Anjos, G. Oliveira, C. Valverde, B. Baseia, H. Napolitano, Synthesis, characterization, and third-order nonlinear optical properties of a new neolignane analogue, R. Soc. Chem. 6 (2016).
- [22] G.C. Ribeiro, L.R. Almeida, H.B. Napolitano, C. Valverde, B. Baseia, Polarization effects on the third-order nonlinear optical properties of two polymorphs of enamine derivative, Theor. Chem. Acc. 135 (2016) 244. https://doi.org/10.1007/s00214-016-1999-1.
- [23] R.F.N. Rodrigues, L.R. Almeida, F.G. dos Santos, P.S. Carvalho, W.C. de Souza, K.S. Moreira, G.L.B. de Aquino, C. Valverde, H.B. Napolitano, B. Baseia, Solid state characterization and theoretical study of non-linear optical properties of a Fluoro-N-Acylhydrazide derivative, PLoS

One. 12 (2017) e0175859. https://doi.org/10.1371/journal.pone.0175859.

- [24] B. Baseia, F. Osório, L. Lima, C. Valverde, Effects of Changing Substituents on the Non-Linear Optical Properties of Two Coumarin Derivatives, Crystals. 7 (2017) 158. https://doi.org/10.3390/cryst7060158.
- [25] C. Valverde, R.F.N. Rodrigues, D.F.S. Machado, B. Baseia, H.C.B. de Oliveira, Effect of the crystalline environment on the third-order nonlinear optical properties of L-arginine phosphate monohydrate: a theoretical study, J. Mol. Model. 23 (2017) 122. https://doi.org/10.1007/s00894-017-3274-3.
- [26] A.N. Castro, F.A.P. Osório, R.R. Ternavisk, H.B. Napolitano, C. Valverde, B. Baseia, Theoretical investigations of nonlinear optical properties of two crystalline acetamides structures including polarization effects of their environment, Chem. Phys. Lett. 681 (2017) 110–123. https://doi.org/10.1016/j.cplett.2017.05.066.
- [27] C. Valverde, W.F. Vaz, J.M.F. Custodio, V.S. Duarte, P.S. Carvalho-Jr, A.S. Figueredo, G.L.B. de Aquino, B. Baseia, H.B. Napolitano, The solid state structure and environmental polarization effect of a novel asymmetric azine, New J. Chem. 41 (2017) 11361–11371. https://doi.org/10.1039/C7NJ00618G.
- [28] L.R. Almeida, M.M. Anjos, G.C. Ribeiro, C. Valverde, D.F.S. Machado, G.R. Oliveira, H.B. Napolitano, H.C.B. de Oliveira, Synthesis, structural characterization and computational study of a novel amino chalcone: a potential nonlinear optical material, New J. Chem. 41 (2017) 1744–1754. https://doi.org/10.1039/C5NJ03214H.
- [29] C. Valverde, F.A.P. Osório, T.L. Fonseca, B. Baseia, DFT study of third-order nonlinear susceptibility of a chalcone crystal, Chem. Phys. Lett. 706 (2018) 170–174. https://doi.org/10.1016/j.cplett.2018.06.001.
- [30] T.L. Fonseca, J.R. Sabino, M.A. Castro, H.C. Georg, A theoretical investigation of electric properties of L-arginine phosphate monohydrate including environment polarization effects, J. Chem. Phys. 133 (2010) 1–8. https://doi.org/10.1063/1.3501237.
- [31] O.L. Santos, T.L. Fonseca, J.R. Sabino, H.C. Georg, M.A. Castro, Polarization effects on the electric properties of urea and thiourea molecules in solid phase, J. Chem. Phys. 143 (2015) 234503. https://doi.org/10.1063/1.4937481.
- [32] D.M. Bishop, D.W. De Kee, The frequency dependence of nonlinear optical processes, J. Chem. Phys. 104 (1996) 9876–9887. https://doi.org/10.1063/1.471752.
- [33] M. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, others, Gaussian 09, revision D. 01, (2009).
- [34] M.S.H. Faizi, N.O. Sharkina, T.S. Iskenderov, Crystal structure of 2-azaniumyl-3-bromo-6-oxo-5,6-dihydropyrido[1,2- a ]quinoxalin-11-ium dibromide, Acta Crystallogr. Sect. E Crystallogr. Commun. 71 (2015) o17–o18. https://doi.org/10.1107/S2056989014026127.
- [35] R.F.W. Bader, A quantum theory of molecular structure and its applications, Chem. Rev. 91 (1991) 893–928. https://doi.org/10.1021/cr00005a013.

- [36] R.F.W. Bader, Atoms in molecules, Acc. Chem. Res. 18 (1985) 9–15. https://doi.org/10.1021/ar00109a003.
- [37] R.F.W. Bader, Atoms in molecules : a quantum theory, Clarendon Press, 1990.
- [38] K. Burke, Perspective on density functional theory, J. Chem. Phys. (2012). https://doi.org/10.1063/1.4704546.
- [39] T. Lu, F. Chen, Multiwfn: A multifunctional wavefunction analyzer, J. Comput. Chem. 33 (2012) 580–592. https://doi.org/10.1002/jcc.22885.
- [40] B. Galdino, D. Oliveira, R. De Cássia, M. Ugulino, D. Araújo, Full Paper Uma comprovação químico-quântica sobre a formação de ligações de hidrogênio e interações secundárias em sistemas heterocíclicos intermoleculares Introdução, 1 (2009) 167–182.
- [41] R.F.W. Bader, The quantum mechanical basis of conceptual chemistry, Monatshefte Fur Chemie. 136 (2005) 819–854. https://doi.org/10.1007/s00706-005-0307-x.
- [42] I. Rozas, I. Alkorta, J. Elguero, Behavior of Ylides Containing N, O, and C Atoms as Hydrogen Bond Acceptors, J. Am. Chem. Soc. 122 (2000) 11154–11161. https://doi.org/10.1021/ja0017864.
- [43] S.R. Prabhu, A. Jayarama, K. Chandrasekharan, V. Upadhyaya, S.W. Ng, Synthesis, growth, structural characterization, Hirshfeld analysis and nonlinear optical studies of a methyl substituted chalcone, J. Mol. Struct. 1136 (2017) 244–252. https://doi.org/10.1016/j.molstruc.2017.01.069.
- [44] E.D. D'silva, G.K. Podagatlapalli, S. Venugopal Rao, S.M. Dharmaprakash, Study on third-order nonlinear optical properties of 4-methylsulfanyl chalcone derivatives using picosecond pulses, Mater. Res. Bull. 47 (2012) 3552–3557. https://doi.org/10.1016/j.materresbull.2012.06.063.
- [45] P.K. Murthy, C. Valverde, V. Suneetha, S. Armaković, S.J. Armaković, N.U. Rani, N.V. Naidu, An analysis of structural and spectroscopic signatures, the reactivity study of synthetized 4,6dichloro-2-(methylsulfonyl)pyrimidine: A potential third-order nonlinear optical material, J. Mol. Struct. 1186 (2019) 263–275. https://doi.org/10.1016/j.molstruc.2019.03.021.
- [46] J.M.F. Custodio, G.D.C. D'Oliveira, F. Gotardo, L.H.Z. Cocca, L. De Boni, C.N. Perez, L.J.Q. Maia, C. Valverde, F.A.P. Osório, H.B. Napolitano, Chalcone as Potential Nonlinear Optical Material: A Combined Theoretical, Structural, and Spectroscopic Study, J. Phys. Chem. C. 123 (2019) 5931–5941. https://doi.org/10.1021/acs.jpcc.9b01063.
- [47] A.N. Prabhu, V. Upadhyaya, A. Jayarama, K. Subrahmanya Bhat, Synthesis, growth and characterization of  $\pi$  conjugated organic nonlinear optical chalcone derivative, Mater. Chem. Phys. 138 (2013) 179–185. https://doi.org/10.1016/j.matchemphys.2012.11.041.
- [48] A.N. Prabhu, V. Upadhyaya, A. Jayarama, K.S. Bhat, Third-order NLO property of thienyl chalcone derivative: Physicochemical analysis and crystal structure determination, Mol. Cryst. Liq. Cryst. 637 (2016) 76–86. https://doi.org/10.1080/15421406.2016.1177921.
- [49] K. Naseema, K.. Sujith, K.B. Manjunatha, B. Kalluraya, G. Umesh, V. Rao, Synthesis, characterization and studies on the nonlinear optical parameters of hydrazones, Opt. Laser Technol. 42 (2010) 741–748. https://doi.org/10.1016/j.optlastec.2009.11.019.

- [50] H.J. Ravindra, K. Chandrashekaran, W.T.A. Harrison, S.M. Dharmaprakash, Structure and NLO property relationship in a novel chalcone co-crystal, Appl. Phys. B. 94 (2009) 503–511. https://doi.org/10.1007/s00340-008-3248-3.
- [51] P. Günter, Nonlinear Optical Effects and Materials, 4th ed., Springer Berlin Heidelberg, Berlin, 2000. https://doi.org/10.1007/978-3-540-49713-4.

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