# Growth, Structural, Second Harmonic Generation and Quantum Chemical Analysis of *N,N'*-Diphenylguanidinium Nicotinate Hydrate

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Solution growth approach was used to create *N,N*-Diphenylguanidinium Nicotinate Monohydrate (DPGNH) single crystals with a fine habitat. X-ray diffraction examination of a single crystal revealed the structural characteristics. Density Functional Theory (DFT) investigations were carried out to divulge the structural, spectral, Frontier Molecular Orbitals (FMO's) and Non-Linear Optical (NLO) properties of *N,N*-Diphenylguanidinium Nicotinate Monohydrate (DPGNH) at molecular level. The molecular structure of DPGNH was optimized utilizing B3LYP/6-31G (d,p) level of theory. This optimized molecular structure was further used to examine the computed UV-vis spectra. The FMO's were further explored to known about the electron transfer within DPGNH molecule. In order to shed light on the Second Harmonic Generation (SHG) at the molecular level, the NLO characteristics were evaluated using DFT. By using the Kurtz-Perry powder approach, the experimental Second Harmonic Generation (SHG) was examined.

Graphical abstract
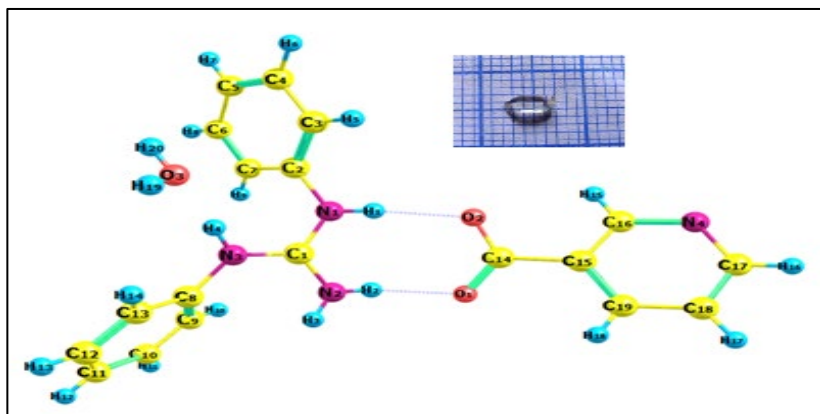
1. Introduction

Non-Linear Optical (NLO) materials have a dielectric polarization that reacts nonlinearly to the incident light's electric field, resulting in a range of frequencies. Such materials are employed in conjunction with lasers to enable the expansion of the laser's spectrum region, which is currently limited. Guanidine derived compounds may be interesting for NLO applications in view of their physical characteristics [1-3]. Due to their D_{3h} symmetry, guanidinium moieties ensure a strong octupolar moment and a modest dipole moment, which prevents big dipolar molecules from forming in centrosymmetric space groups (that extinguish the non-linear optical responses to stimuli). *N,N'*-diphenylguanidine a whippy molecule showing discernible polar and apolar groups and their aromatic rings could be self-

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assembling through π-π cooperation [4]. Based on this the explore for new *N,N'*-Diphenylguanidine based single crystal showing good SHG activity has expanded. Normally, excessively clear from the past reports [4-7]. Density Functional Theory (DFT) has turn out to be a plan of action for foreseeing the molecular belongings of large molecular frameworks [8]. DFT contends well in precision, for most systems, with simple wave functions-based methods. Additionally, the cost viability of DFT renders it a very practical method for computing the properties of molecular systems [9]. In micro scale opinion, the portrayal of second order susceptibility ($\chi^{(2)}$) is cognate to the molecular response as the so called first hyperpolarizability (β). In this present research, crystal growth, structural, spectral, frontier molecular orbitals and non-linear optical properties of *N,N'*-diphenylguanidinium nicotinate hydrate (DPGNH) have been explored in detail for further research and applications in near future.

2. Material and Methods

The fine habitat single crystals of *N,N'*-diphenylguanidinium nicotinate hydrate (DPGNH) was developed by slow evaporation technique. Equimolar quantities of *N,N'*- diphenylguanidine (Hi-Media, AR grade) and Nicotinic acid (Loba chemie, AR grade) were used to develop the single crystals of DPGNH. The determined amount of nicotinic acid and *N,N'*-diphenylguanidine were disintegrated in mixed solvent of distilled water + ethanol (0.25:0.75) ratio. The resulting solution was continuously permitted to stir using an immersible magnetic stirrer for about 4 hours to achieve homogeneous solution. The homogeneous solution was then leached into clean beaker using whatmann filter paper and was covered with aluminum foil with perforation at the top to let the solution evaporate under ambient conditions. Good faceted highly transparent optical quality single crystals of the titular material were harvested after a period of 14 days. The snapshot of the as grown DPGNH single crystal is depicted in Fig. 1.
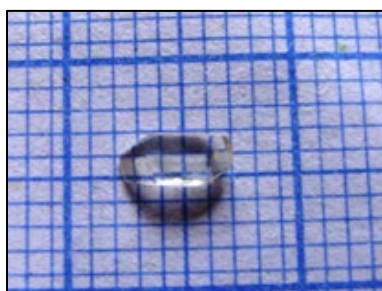

Fig. 1. Snapshot of as grown DPGNH single crystal.

2.1 Computational Details

Through the B3LYP/6-31G (d,p) level of theory, all calculations were carried out by the Gaussian 09 program [10-12].

3. Results and Discussion

3.1 Single Crystal X-ray Diffraction Study

A single crystal X-ray diffraction investigation on the DPGNH crystal was conducted to shed light on the lattice parameters and crystal structure. The research reveals that the titular material crystallizes in an orthorhombic crystal structure with the non-centrosymmetric space group $P2_12_12_1$. Additionally, it was determined that the DPGNH single crystal's acquired lattice parameters, *a* = 10.25 (3) Å, *b* = 11.67 (2) Å, and *c* = 15.89 (2) Å, were in good agreement with the results presented in the published literature [13].

3.2 Molecular Structure Commentary

In order to facilitate the SHG action, the material must own a complete figure of the susceptibility which is a bulk belonging and generally collaborated with non-centrosymmetric framework. The crystal structure of DPGNH was reported by M. R. Silva et al. [13]. It is obvious from the report [13], that DPGNH solidifies in non-centrosymmetric space group $P2_12_12_1$. Thereby satisfying the initial screening for existence of SHG at molecular level and in bulk. The DPGNH is found to have a three-dimensional hydrogen bond organizing anions, cations and water molecules consequently re-upholding the crystal cohesion. The water molecule structure criss-cross chains along with the nicotinate ions and these chains are then interconnected by hydrogen bonds through guanidinium sections. In the crystalline phase, the titular material has an acentric packing of four molecules per unit cell with the hydrogen bonds between the N-H group of diphenylguanidinium cation and carboxylate (COO⁻) group of nicotinate entity. Additionally, there are a few C-H...π intermolecular interactions. Such interactions utilize the π cloud of the aromatic rings as acceptors for the hydrogen protons. Some selected H-bonding geometry for the titular material is represented as follows, (N2-H2-O1), N2 – H2 (0.859 Å), H2...O1 (1.934 Å). Similarly, for (N1-H1-O2) N1 – H1 (0.860 Å), H1...O2 (1.983 Å) [13]. According to the through structural examination from the reported data [13] it may possible to improve the SHG nonlinearity for the titular material due to the cooperative action of polarizable cations. Moreover, the donor-acceptor system's hyperpolarizability has grown due to the afore mentioned strong hydrogen bonding in the coordinated linkers [14-18]. In order to compute and estimate the several properties of DPGNH at molecular level, the Crystallographic Information File (CIF) ((CCDC deposit number: 724892)) [13] was utilized as code to stream line the molecular geometry of DPGNH. The streamlined molecular structure of DPGNH was found to be in line with the experimentally reported structure with slight deviations in adequate range [13]. The streamlined molecular structure of DPGNH is presented in Fig. 2.
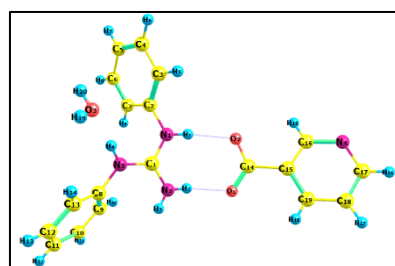

Fig. 2. Streamlined molecular structure of DPGNH.

3.3 UV-vis Spectral Scrutiny

UV-vis spectral scrutiny is one of the effective aids to screen the NLO materials for their employability in terms of device-oriented applications. For a NLO material, there should not be any significant figure of absorption in the active window

especially in the operating wavelength of 532 nm. In turn, they mean a high transmittance range. In order to explore the UV-vis spectrum of DPGNH at molecular level, TD-DFT at B3LYP/6-31G (d,p) level in vapor stage was employed. The input geometrical parameters were derived from the streamlined molecular geometry. The computed UV-vis spectrum of DPGNH is presented in Fig. 3. It is derived from, Fig. 3, that the maximum absorption occurs at 316.95 nm. Above this excitation energy there is no significant absorption in the window.
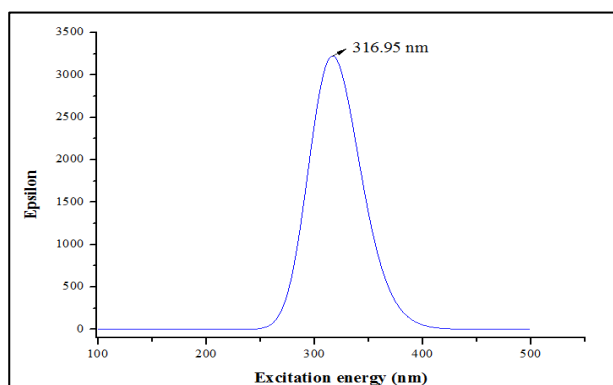

Fig. 3. Computed UV-vis spectrum of DPGNH molecule.

3.4 Frontier Molecular Orbitals

Frontier molecular orbitals are purported, Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO). The energy gap (ΔE_g) separating the HOMO and LUMO is useful parameter in theoretical assessments in providing clear features on optical and electrified conditions. The exchange of charge between the HOMO-LUMO energy states contributes towards the NLO response at molecular level as well as the concoction solidness of molecules. The HOMO spoke to as electron contributor whose energy is identified with ionization potential. The LUMO spoke to as electron receiver whose energy is related to electron affinity. The HOMO-LUMO plots of DPGNH molecule is presented in Fig. 4. The HOMO being an electron contributor is spread over nicotinate anions. LUMO being an electron acceptor is principally localized over the entire *N,N'*-diphenylguanidinium fragment. This electron transfer from the nicotinate to *N,N'*-diphenylguanidinium moiety happens by the way of the hydrogen bonds framed by means of the water molecule. It is likewise observed, from the HOMO-LUMO plots that, the LUMO additionally delocalizes on the oxygen atom of water molecule as well as the oxygen atoms of nicotinate anions. The global chemical reactivity descriptors for DPGNH molecule have been calculated using Koopmans's hypothesis and standard relations [19,20] and are introduced in Table 1.
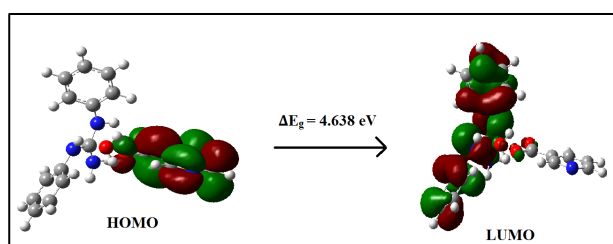

Fig. 4. HOMO-LUMO plots of DPGNH molecule.

Table 1. List of global chemical reactivity descriptors for DPGNH molecule.

Parameters	B3LYP/6-31G(d,p)
E_{HOMO} (eV)	-5.789
E_{LUMO} (eV)	-1.151
ΔE_{gap} (eV)	4.638
Ionization potential (IP) (eV)	5.789
Electron affinity (EA) (eV)	1.151
Chemical potential (μ) (eV)	-3.470
Chemical hardness (η) (eV)	2.319
Global softness (s) (eV^{-1})	0.215
Electronegativity (χ) (eV)	3.470
Electrophilicity index (ω) (eV)	2.596

3.5 Molecular Electrostatic Potential (MEP) Analysis

Molecular Electrostatic Potential (MEP) surface analysis represent the ions dispersal of molecule in a three-dimensional way which permits one to picture the variably charged districts of a molecule and also to acknowledge the reactive nature of molecule. The MEP surface analysis are the plot of electrostatic potential planned onto the iso-electron density surface which at the same time show the molecular shape, size and electrostatic potential values of DPGNH molecule. The shading reviewing is utilized to perceive the presence of charges in the electrostatic potential regions of a molecule. The blue regions of the molecules exhibit the strongest attraction and were inclined to nucleophilic assault, while red regions indicate the strongest dismissal and are related with electrophilic assault. The prevailing of green regions in the MEP surfaces speaks to an expected somewhere between the two extremes red and dark blue color. The MEP of DPGNH molecule was obtained with iso-surface value from -0.166e0 to +0.166e0. The MEP surface analysis illustrates the charge transfer taking place within DPGNH molecule. The MEP surface analysis of DPGNH molecule is shown in Fig. 5.
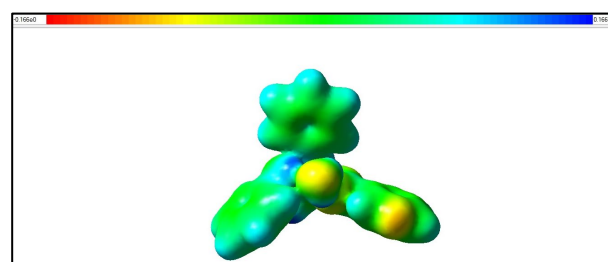

Fig. 5. MEP surface analysis of DPGNH molecule.

3.6 Non-Linear Optical Calculations

So as to toss light on the linear and non-linear optical features of DPGNH at molecular level, the DFT estimations were done using B3LYP/6-31G (d,p) baseline point. It is important that the NLO action of a given material is higher when they have non-zero qualities and has high dipole moment, high linear polarizability and high hyperpolarizability. The total static dipole moment 'μ', average linear polarizability '$\langle\alpha\rangle$' and molecular static first hyperpolarizability 'β_{total}' of DPGNH molecule have been calculated using standard relations [20].

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

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

$$\beta_{total} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

As the Gaussian 09 assessments of the linear and non-linear optical parameters are counted in a.u., the assessed values are converted into e.s.u. using the transformations as ($\langle\alpha\rangle$: 1 a.u. = 0.1482 × 10-24 e.s.u.; β_{total} : 1 a.u. = 8.6393 × 10-33 e.s.u.). The assessed values of total static dipole moment 'μ', average linear polarizability '$\langle\alpha\rangle$' and molecular static first hyperpolarizability 'β_{total}' for DPGNH molecule were discovered to be 3.6621 Debye, 37.358 × 10^{-24} e.s.u. and 8.311 × 10^{-30} e.s.u. independently. This not zero and critical figures of the before referenced linear and non-linear parameters communicates the NLO actions of DPGNH at molecular level. The linear and non-linear optical parameters of the titular material calculated utilizing B3LYP/6-31G (d,p) level reached from finite-field proposition are introduced in Table 2.

Table 2. Linear and non-linear optical parameters for DPGNH molecule.

Parameters	B3LYP/6-31G (d,p)
Dipole moment	
μ_x	-3.2313
μ_y	0.8977
μ_z	-1.4710
μ_{total} (Debye)	3.6621
Polarizability	
α_{xx}	261.715
α_{yy}	240.469
α_{zz}	1.980
$\langle\alpha\rangle \times$ **10^{-24} e.s.u.**	**37.358**
Hyperpolarizability	
β_{xxx}	- 920.605
β_{xxy}	83.591
β_{xyy}	- 26.204
β_{yyy}	- 636.603
β_{xxz}	47.284
β_{xyz}	- 120.506
β_{yyz}	69.451
β_{xzz}	68.791
β_{yzz}	183.344
β_{zzz}	17.100
$\boldsymbol{\beta_{total}} \times$ **10^{-30} e.s.u.**	**8.311**

Bold emphasis the total values of $\langle\alpha\rangle$ and β_{total} are expressed in (e.s.u.) as Gaussian 09 outputs are obtained in (a.u.)

3.7 Second Harmonic Generation (SHG) Analysis

The existence of SHG in the titular material was screened employing Kurtz and Perry powder technique [21]. This procedure permits the assurance of the SHG execution of novel materials comparable to standard SHG material, potassium dihydrogen phosphate (KDP). A Q-switched Nd:YAG laser working at 1064 nm wavelength and 10 ns pulse width and repetition rate of 10 Hz was used to probe the SHG analysis of the titular material. Both the crystalline samples of DPGNH and reference material KDP were stuffed in separate micro-capillary tubes, individually. The yield may well be viewed as a shining green streak emanation with the escalated 532 nm wavelength. The SHG yield was then transformed into equivalent electrical signal and was set out on a digital storage oscilloscope. The optical wave occurrence on photomultiplier tube was transfigured into voltage yield. The SHG wave intensity of 5.8 mV was registered for DPGNH crystalline sample whilst KDP powdered sample was 5.9 mV

for an input energy of 2.7 mJ/pulse was achieved. Thus, the SHG nonlinearity of DPGNH crystalline sample is approximately 0.98 times that of KDP

4. Conclusions

Good quality single crystal of *N,N'*-diphenylguanidinium nicotinate hydrate was developed by mixed solvent of water+ethanol (0.25+0.75) ratio involving slow evaporation technique. The single crystal X-ray diffraction analysis revealed that DPGNH crystallizes in *P2$_1$2$_1$2$_1$* non centrosymmetric space group with orthorhombic crystal system. The molecular structure of DPGNH was optimized utilizing the CIF as info employing B3LYP/6-31G (d,p) baseline. The optimized structure was established to be in acceptable concurrence with the reported crystal structure. The UV-vis spectrum of DPGNH was computed by TD-DFT at the same level of baseline point. The computed UV-vis spectrum revealed that there is no significant absorption in the operating region. The frontier molecular orbitals were inspected. It uncovered the exchange of charge within DPGNH molecule and affirms the NLO activity at molecular level. The MEP surface analysis is presented with shading review and is discussed. The linear and non-linear parameters for DPGNH were estimated at molecular level to explore the NLO response. It was found from the estimations that the DPGNH molecule exhibits decent values. In order to explore the second harmonic generation (SHG) response of titular material, it was subjected to Kurtz-Perry powder analysis. The analysis put forward that DPGNH is found to exhibit SHG nonlinearity almost equivalent to that of the standard reference material potassium dihydrogen phosphite (KDP). The promising crystal growth, crystal structure, crystallization in non-centrosymmetric space group, good values of absorption, charge transfer, good molecular and chemical stability in terms of energy gap, non-zero estimations of NLO properties and promising SHG nonlinearity places DPGNH as an appropriate competitor in the field of NLO.

Acknowledgments

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