Assessment of nonlinear optical response of
3-(4-chlorophenyl)-1-(pyridin-3-yl) prop-2-en-1-one
based on Quantum chemical computations with
different functional and basis sets

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Abstract
Recent research works on chalcone derivatives has proved that they are
potential candidate for optoelectronic and switching devices due to their high
non-linear optical (NLO) response. In the present study, the one of the
chalcone derivatives named 3-(4-chlorophenyl)-1-(pyridin-3-yl) prop-2-en-1-
one (CPP) has been investigated by quantum chemical calculations.
Quantitative assessment of NLO properties of the material has been done with
the help of different theory functional viz. Hartree–Fock, density functional
theory, and Möller–Plesset and basis sets. The parameters which determine
the NLO efficacy of the molecule such as molecular dipole moment,
polarizability, static first and second order hyperpolarizability and HOMO-
LUMO energy gap of the compound have been calculated using a series of
basis sets including polarized and diffuse functions at different levels of
approximation in order to assess the impact of including electron correlation.
The results obtained in this study reveal that compound has an absolute
predominant second harmonic generation efficiency as it has large second-
order hyperpolarizability. A trade-off between accuracy of results and
computation levels has been found. The hyperpolarizability values show that
the compound can respond to an external electric field and possesses efficient
second (SHG) and third (THG) harmonic generation.

Keywords: Dipole moment; Polarizability; Hyperpolarizability; Density
functional theory; MP2

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1. INTRODUCTION

The NLO impact on science is extensively understood. The discovery of nonlinear optical (NLO) phenomena has led to various technological and scientific advances in the fields of understanding in chemistry, physics, biology, and medicine. The exploitation of nonlinear optical effects has made possible numerous areas of research and innovation such as high-intensity physics, frequency metrology, harmonic generation and frequency mixing, optical signal processing, photochemistry, commercial lasers, telecommunications, sensors, environmental monitoring, medicine, manufacturing and materials processing, scientific instrumentation and quantum information science[1]. The applications of NLO is increasing in our daily life as we can notice several applications that have changed our life e.g. the fiber optical cables are the backbone of the internet and communication systems, laser-based medical equipment and analysis tools, monitoring of environmental pollution in the more precise way [2].

There are numerous materials exhibits NLO activity. Organic NLO molecules possess particular π-conjugated systems linking a donor (D) and an acceptor (A) group show large NLO response due to an increasing charge transfer possibility between the π-conjugated aromatic rings. Intramolecular charge transfer (ICT) is the characteristics of these molecules. In consequence of this, the large dipole moments, polarizability and molecular hyperpolarizabilities are observed in these molecules [4-5]. Chalcone are obtained by reacting aromatic aldehydes with aromatic ketones and also known as 1,3-diaryl-propene-1-one. They are open-chain flavanoids possessing a basic structure of two aromatic rings linked by a three carbon α,β-unsaturated carbonyl system.

![Figure 1: Optimized molecular structure of CPP](image)

Hence, the chalcone and their derivatives are found to be very useful material for the applications where the NLO properties play a vital role. The aromatic rings can be easily modified or specific functional group substitutions can be made on the aromatic
ring. Thus modifying the geometry can help to change the NLO activity of chalcone [6]. This makes chalcone very important for NLO studies and therefore, a theoretical and computational study of the NLO behaviour of chalcone will provide an idea to the experimental scientists to modify the geometry of the molecule to suit the required values of NLO properties. The present study comprise of the theoretical assessment of nonlinear optical behaviour of 3-(4-chlorophenyl)-1-(pyridin-3-yl) prop-2-en-1-one (CPP). This is a donor-π-acceptor (D-π-A) type pyridine substitution. The chlorine group acts as an electron donor while pyridine group along with the carbonyl group acts as an electron acceptor. The molecule is non-centrosymmetric in nature which is one of the main criterion for a crystal to have ability to exhibit the Second Harmonic Generation (SHG). The planer structure of the molecule increases the donor-acceptor interactions within the molecule which increases the amount of molecular charge transfer and the degree of nonlinearity.

2. THEORETICAL AND COMPUTATIONAL BACKGROUND
When an intense electric field is applied to an isolated molecule, the dipole moment may be expressed as a Taylor series
\[ \mu_i = \mu_i^0 + \alpha_{ij} E_j + \frac{1}{2!} \beta_{ijk} E_j E_k + \frac{1}{3!} \gamma_{ijkl} E_j E_k E_l + \ldots \]
where \( \mu_i^0 \) is the static dipole moment, \( \alpha_{ij} \) is the linear (or first-order) polarizability, \( \beta_{ijk} \) is the second-order polarizability (or first hyperpolarizability), and \( \gamma_{ijkl} \) is the third-order polarizability (or second hyperpolarizability).

The NLO activity of a compound is due to hyperpolarizabilities of p electrons. Due to the application of an electric field, a force is experienced by charge distribution systems that cause displacement of the electron density. This displacement causes induced polarization or induced dipole. The polarization \( P \) under the electric field is given by,
\[ P_i = P_i^0 + \chi_{ij}^{(1)} E_j + \frac{1}{2!} \chi_{ijk}^{(2)} E_j E_k + \frac{1}{3!} \chi_{ijkl}^{(3)} E_j E_k E_l + \ldots \]
where \( P_i^0 \) is the static polarization, \( \chi_{ij}^{(1)} \) is the linear susceptibility, and \( \chi_{ijk}^{(2)} \) and \( \chi_{ijkl}^{(3)} \) are the second and third susceptibility, respectively. This equation may also be expressed as,
\[ P = (P_0 + \frac{1}{4} \chi_{i}^{(2)} E_i^2) + \chi_{i}^{(1)} E_0 \cos \omega t + \frac{1}{4} \chi_{i}^{(2)} E_0^2 \cos 2\omega t + \ldots \]
The first term represents a second-order contribution to the static polarization. The second term is a frequency component \( \omega \) corresponding to the incident light frequency. The third term shows a new component of frequency 2\( \omega \), which means that incident light beam produces light at twice the input frequency after passing through a second-order NLO material.
The optimized geometrical parameters of the molecule were computed by the DFT method using the Gaussian 09 program [7] package employing 6-311++G(d,p) basis set and Becke’s three parameter (local, nonlocal, Hartree–Fock) hybrid exchange functional with Lee–Yang–Parr correlation functional (B3LYP) [8–10]. The basis set 6-311++G(d,p) augmented by d polarization functions on heavy atoms and p polarization functions on hydrogen atoms as well as diffuse functions for both hydrogen and heavy atoms were used [11,12].

3. RESULT AND DISCUSSION
3.1. Geometry optimization
The ground state optimized structure of 3-(4-chlorophenyl)-1-(pyridin-3-yl) prop-2-en-1-one CPP is shown in Figure 1. The molecule consists of pyridine ring and chlorophenyl ring connected with -C=O- group. The initial geometry taken from crystallographic information file (CIF) of CPP was minimized without any constraint using B3LYP/6-311++G(2d,p) level of theory and the optimized structural parameters were obtained. From the theoretical values, it is found that some values slightly deviates from the experimental values. These differences are probably due to intermolecular interactions in the solid state. This structure is remarkably similar to one of the crystallographic asymmetric unit and hence these structural parameters are the basis for the calculation of the other parameters. The optimized and experimental structures of the molecule were compared by superimposing them using a least-squares algorithm that minimizes the distances between the corresponding non-hydrogen atoms as shown in Figure 2. The self-consistent field energy of the stabilized geometry of the molecule, calculated by DFT method is -1129.8904 au and the calculated dipole moment is 0.3539 Debye.

![Figure 2](image)

**Figure 2:** Comparison of the experimental (GREEN) and optimized structure(RED) OF CPP.

The molecular structure consists of two rings which are planar with dihedral angle C19-C18-C16-C14 = -179.8309 and C8-C10-C13-C14= -171.7165. Due to high electronegativity of the oxygen than carbon, the carbonyl group is polar and has
Assessment of nonlinear optical response of 3-(4-chlorophenyl)-1-(pyridin-3-yl). substantial dipole moments. The carbonyl group is also planar with respect to the Ring2 with a dihedral angle O2-C13-C10-C11= -171.2671. Such planar structure increases electron negativity within the π-conjugated molecular system, which results in nonlinearity of the molecule.

3.2. Energy Gap

Band gap in π-conjugated system is a practically important subject. Materials of low band gap are of interest for their intrinsic conductivity in electronic and photonics devices such as light emitting diodes and solar cells. The Band gap is defined as the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels in the molecular system [14], i.e. \(E_g = E_{LUMO} - E_{HOMO}\) (EV)

Table 1 summarizes the self-consistent field (SCF) energies and the energy band gap of CPP at HF, DFT and MP2 methods with various combinations of basis sets. Energies and energy gap of the titled molecule for different basis sets and methods have been displayed in Figure 3 and Figure 4, respectively.

**Table 1**: Self consistent field energy (SCF) and HOMO–LUMO GAP of CPP at HF, DFT (B3LYP) and MP2 levels of theory

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<th>SCF(au)</th>
<th>GAP(au)</th>
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The energy gap values obtained from HF and MP2 methods are close to each other. In both the HF and MP2 methods, the energy gap was calculated to be minimum as \(~0.35\) a.u. (Figure 4). In the case of DFT method, the curve shows the same tendency but the computed values were approximately 45% lower than those calculated from HF and MP2 methods. The hydrogen-bonded molecular crystals commonly have lower energy gap than an isolated molecule in the gas phase. This is due to fact that hydrogen bond interactions between the electron donor and acceptor may tend to decrease the energy gap [15].

![Graph showing energy gap for different methods](image)

**Figure 3:** Basis set Vs SCF energy for the molecule CPP

As expected, the energy band gap of CPP monomer is overestimated while comparing with the experimental value because the correlation contribution is neglected. The estimation of accurate band gap is obtained by applying a higher level basis set using diffused and polarization functions. The DFT (B3LYP) method along with 6-311++g(2d,p) basis set yielded a good agreement with the experiment [16], the absolute error is 0.98 eV.
3.3. Nonlinear properties
Quantum chemical calculations have been very useful for predicting the molecular NLO properties of active compounds [17,18]. Hyperpolarizability is useful in understanding the relationship between the molecular structure and nonlinear optical properties. The hyperpolarizability of the title molecule has been investigated using the keyword “Polar” in the Gaussian 09 software at different levels of theory. The total static dipole moment ($\mu$), the mean polarizability ($\alpha_{\text{tot}}$), the anisotropic polarizability ($\Delta \alpha$), the mean first-order hyperpolarizability ($\beta$) and the mean static second-order hyperpolarizability ($\gamma$) for CPP have been calculated by using the following questions [19,20] and summarized in Table 2.

\[\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad \text{(i)}\]

\[\alpha_{\text{tot}} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad \text{..........................(ii)}\]

\[\Delta \alpha = 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2} \quad \text{.................................(iii)}\]

\[\beta_{\text{tot}} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zzx} + \beta_{zyy})^2]^{1/2} \quad \text{...............(iv)}\]
\[ \gamma_{tot} = \left( \frac{1}{3} \right) [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})] \] .................(v)

The conversion factor of \(\alpha\), \(\beta\) and \(\gamma\) in atomic unit are 1 atomic unit (a.u.) = 0.1482 x 10\(^{-24}\) electrostatic unit (esu) for \(\alpha\), 1 a.u. = 8.6393x10\(^{-33}\) esu for \(\beta\) and 1 a.u. = 5.0367x10\(^{-40}\) esu for \(\gamma\).

**Table 2:** Total dipole moment (\(\mu\)), polarizability (\(\alpha\)) first hyperpolarizability (\(\beta\)) and second hyperpolarizability (\(\gamma\)) of CPP at HF, DFT (B3LYP) and MP2 levels of theory

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<th>(\beta_{tot}) (au)</th>
<th>(\gamma_{tot}) (au)</th>
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</tbody>
</table>

The dipole moment of the titled molecule for different levels of theory and basis set are presented in Figure 5. It is clear that the molecule has a non-zero dipole moment and the increase of the basis sets size tends to achieve the convergence and therefore to obtain reliable values of dipole moment. At HF, it is clear that the convergence is achieved when both the diffused and the polarization functions are included in the basis set. The calculated parameters from HF are similar to the parameters obtained from MP2 and larger than those obtained from DFT with the advantage of less computational cost.
Figure 5: Dipole moment Vs Basis set for the molecule CPP at different level of theory

Polarizability is described by a second rank tensor. Its average value ($\alpha_{\text{total}}$) can be obtained by considering only the diagonal elements as given by equation (ii). The calculated $\alpha$ values are given in Table 2 and graphically presented in Figure 6. It is clear from the graph that the larger values of $\alpha_{\text{total}}$ are obtained for more diffuse and polarization functions. The values at HF level are almost same for higher basis sets except at cc-pvdz basis set where the value is 0.58% higher than the value obtained at the 6-311++g(2d,p) basis set.

At the same time, the values obtained from MP2 are unerringly similar to those obtained from HF. The DFT values are 0.97% to 2.97% higher than those obtained from HF/MP2. Therefore, the results suggested that at any level of theory, the 6-311++g(2d,p) basis set most likely calculates the similar values.

Figure 6: Polarizability Vs Basis set for the molecule CPP at different level of theory
The first hyperpolarizability is responsible for the second-order nonlinear optical properties as SHG; therefore suggest the possibility of technological applications of the molecule. The $\beta$ values is represented by a third rank tensor. The 27 components of the 3D matrix can be reduced into 10 components according to Kleinman symmetry [21]. The output file of Gaussian 09W provides the main ten components ($\beta_{xxx}$, $\beta_{xxy}$, $\beta_{xyy}$, $\beta_{yyy}$, $\beta_{xxz}$, $\beta_{xyz}$, $\beta_{yyz}$, $\beta_{xzz}$, $\beta_{yzz}$, $\beta_{zzz}$). The magnitude of the first hyperpolarizability ($\beta_{\text{total}}$) can be defined in terms of the x, y, z components as given in relation (iv) [22]. The computed $\beta_{\text{total}}$ values are given in Table 2 and graphically presented in Figure 7. By observing this Figure, it is clear that the values obtained from DFT are about 20\% lower than those obtained from HF and the values obtained from MP2 are exactly similar to those obtained from HF. On the other hand, it is also clear that at HF and DFT methods the convergence could be achieved with basis sets having polarized and diffused functions. Urea is the reference molecule which is used in the study of the NLO properties of molecular systems. Therefore, it is used commonly as a threshold value for comparative purpose. Calculated $\beta_{\text{total}}$ value for the title molecule is found to be $\sim$ 5 to 7 times (5 times using HF/MP2 and 7 times using DFT) greater than the $\beta_{\text{total}}$ value of urea ($0.1947 \times 10^{-30}$ esu).

The second hyperpolarizability is responsible for the third order nonlinear optical properties as THG; therefore suggest the possibility of technological applications of the molecule. The $\gamma (0,0,0)$ and $\gamma (-3\omega,\omega,\omega)$ values describe the static second hyperpolarizability at $\omega = 0$ frequency, and the dynamic hyperpolarizability at $\omega$ frequency. The average value of the $\gamma$ is given by relation (v). The computed $\gamma$ values are given in Table 2 and graphically presented in Figure 8. It is clear that the values obtained from HF and MP2 are similar and the values at DFT level are close to the values obtained at
HF/MP2 except for 6-311++g(2d,p) and cc-pvdz basis sets. It is observed that the HF and MP2 values of the nonlinear optical parameters are comparable (similar) to each other. This is mainly due to the cancellation of errors in the HF method and the basis set effect which even gave HF values in smaller basis closer to the experiment. This study shows that the MP2 and the HF methods give similar results as far as the nonlinear optical parameters of CPP is concerned. However, a sudden change in the value of second-order hyperpolarizability has been observed in Figure 8 at DFT/B3LYP level for 6-311++g(d,p) and 6-311++g(2d,p) basis set. This shows that the second-order hyperpolarizability values are very sensitive to the selection of the basis set.

![Figure 8: Second order hyperpolarizability Vs Basis set for the molecule CPP at different level of theory](image)

4. CONCLUSION
In this work, the NLO properties of CPP were investigated using HF, DFT and MP2 methods with different basis sets. The linear and nonlinear parameters such as dipole moment, polarizability and hyperpolarizabilities were computed. The study shows that the MP2 level of theory does not provide better nonlinear parameters. HF method also produces the same result compared to the MP2 method at lower computational cost. Basis set having both the diffusion and polarisation functions must be taken into consideration for the computation of hyperpolarizabilities. Calculated first order hyperpolarizability value for the title molecule is found to be ~ 5 to 7 times greater than the βtotal value of urea. The parameters like dipole moment, polarizability, first hyperpolarizability and second hyperpolarizability showed that chalcone derivative CPP can respond to an external electric field and allow efficient SHG and THG. Therefore, the compound seems to have potential candidature in the field of nonlinear optics.
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REFERENCES
