# DFT studies on Vibrational, NLO, Thermal and Energy Gap studiesof 4-(3-clorophenyl)-2-phenyl-1,3-thiazole(Cl-PPT)

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*Abstract*: --- DFT studies have been carried out on CL-PPT using DFT-B3LYP/6-311+Glevel of the theory. The structural parameters of the title molecule, like bond length, bond angle and dihedral angles have been calculated and compared with available experimental data. The FTIR wavenumbers are calculated using above mentioned method and compared with the experimental IR wave numbers. Nonlinear optical properties and thermal properties have been calculated using the same methodology. The frontier molecular orbital studies have been carried out to explain the charge transfer in title molecule.From this analysis, it can be seen that the vibrational frequencies obtained from B3LYP method are in good agreement with the experiment.

*Keywords* ⎯ FT-IR spectra, Hyperpolarizability, Homo-Lumo energy gap, DFT..

## I. INTRODUCTION

Thiazoles that contain sulfur atom are important class of heterocyclic compounds. These are present in many natural/synthetic products, which have a wide range of pharmacological activities [1] and also find various applications in the other fields such as polymers [2], liquid crystals[3]. Due to its fascinating biological activity, it is very interesting to study the geometrical, vibrational, thermal and nonlinear optical properties of the title molecule. Density functional theory (DFT) is becoming more useful to experimentalists in computing the geometrical parameters and other properties like vibrational, thermal, nonlinear, optical etc. of polyatomic molecules[4].

The title molecule (fig. 1.) considered for this study has been synthesized previously and reported by Pavan Kumar etal[5]. The geometrical parameters (like bond lengths, bond angles and dihedral angles), non-linear optical properties (like dipole moment, first hyperpolarizability and total hyperpolarizability), thermodynamic parameters (like total energy (Etot), zero-point vibrational energy (ZPVE), heat capacities (CV), entropy (S), total thermal energy ($\square$ tot), rotational constants (rC) and rotational temperatures (rT) and HUMO-LUMO gap energy (ΔEg) have been calculated theoretically and reported. The effect of temperature on some thermodynamic properties at various temperatures have been calculated theoretically and reported.

## II. COMPUTATIONAL DETAILS

The Optimized structure parameters and vibrational frequencies of CL-PPT have been studied by B3LYP methodusing 6-311+G basis set.The quantum chemical calculations have been performed with Gaussian 03W software [6].During optimization the atomic positions of the molecule in all possible geometrical conformations have been fully relaxed, and only the lowest-lying minima is reported. Frequency calculations have been carried out to ensure that the optimized geometry has all positive frequencies and thus is a minimum on the potential energy surface.In scaled quantum mechanical method, the systematic errors of the computed harmonic force field are corrected by a few scale factor (0.97) which are found to be well transferable between chemically related molecules and were recommended for general use [7]The assignments of the calculated wave numbers are made with a high degree of confidence by the VEDA 4 program [8] and animation option of Gauss View 3.0 package which gives a visual presentation of the vibrational modes and frontier molecular orbitals like HOMO and LUMO [9].

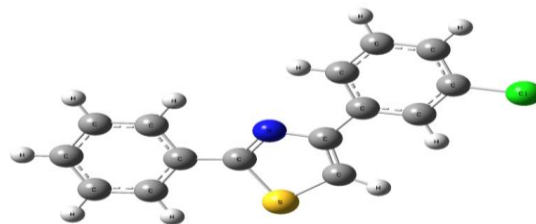## III. GEOMETRIC STRUCTURAL ANALYSIS



*Fig.1 Geometrical structure of ClPPT*

Since the molecular parameters are controlled by the molecular geometry, the crucial step for the calculation of IR spectra is the geometry optimization of the molecule. The optimized bond length, bond angle and dihedral angles of CL-PPT are listed in Table 1. All the bond lengths in thiazole ring are in the range of 1.85 – 1.30Å which are in good agreement with the reported data for thiazole [5] and substituted thiazole [5] and bond lengths in $C_6H_5$part of thetitle molecule are in the range 1.39-1.41 Å which are in good agreement with reported values of benzene and substituted benzenesin literature [10].

**Table. 1: The geometrical parameters of the CL-PPT at B3LYP/6-311+G level**

| Bond length(Å) | | Bond angle (°) | | | | Dihedral angle (°) | |
|---|---|---|---|---|---|---|---|
| R(1-4) | 1.85 | A(4-1-6) | 122 | A(14-12-17) | 118.4 | D(1,6,2,7) | 179.9 |
| R(1-6) | 1.3 | A(4-1-18) | 87 | A(12-14-16) | 116.7 | D(6,2,7,8) | 0.025 |
| R(1-18) | 1.46 | A(1-4-3) | 125.8 | A(19-18-20) | 120.5 | D(2,7,8,10) | 179.9 |
| R(2-3) | 1.37 | A(6-1-18) | 114.6 | A(18-19-21) | 120.1 | D(10,14,12,17) | 179.9 |
| R(2-6) | 1.4 | A(1-6-2) | 119.1 | A(18-19-22) | 120.9 | D(2,7,9,12) | -179.9 |
| R(2-7) | 1.48 | A(1-18-19) | 122 | A(18-20-23) | 120.3 | D(4,3,2,7) | -179.9 |
| R(3-4) | 1.79 | A(1-18-20) | 114.4 | A(18-20-24) | 119.6 | D(3,4,1,18) | -180.0 |
| R(3-5) | 1.07 | A(3-2-6) | 127 | A(21-19-22) | 119.3 | D(1,18,20,23) | 180.0 |
| R(7-8) | 1.41 | A(3-2-7) | 111.7 | A(19-21-25) | 119.2 | D(1,18,19,21) | 180.0 |
| R(7-9) | 1.41 | A(2-3-4) | 129.4 | A(19-21-26) | 119.6 | D(2,6,1,18) | -179.9 |
| R(8-10) | 1.39 | A(2-3-5) | 118.6 | A(23-20-24) | 120 | D(6,2,7,9) | -178.3 |
| R(8-11) | 1.08 | A(6-2-7) | 120.1 | A(20-23-25) | 119.7 | | |
| R(9-12) | 1.39 | A(2-7-8) | 121.2 | A(20-23-27) | 119.2 | | |
| R(9-13) | 1.08 | A(2-7-9) | 118.9 | A(25-21-26) | 120.2 | | |
| R(10-14) | 1.4 | A(4-3-5) | 118.7 | A(21-25-23) | 120.1 | | |
| R(10-15) | 1.08 | A(8-7-9) | 120.5 | | | | |
| R(12-14) | 1.39 | A(7-8-10) | 118.8 | | | | |
| R(12-17) | 1.08 | A(7-8-11) | 119.8 | | | | |
| R(14-16) | 1.41 | A(7-9-12) | 120.8 | | | | |
| R(18-19) | 1.41 | A(7-9-13) | 120.8 | | | | |
| R(18-20) | 1.39 | A(10-8-11) | 120.8 | | | | |
| R(19-21) | 1.39 | A(8-10-14) | 119.8 | | | | |
| R(19-22) | 1.08 | A(8-10-15) | 119.3 | | | | |
| R(20-23) | 1.4 | A(12-9-13) | 121.8 | | | | |
| R(20-24) | 1.08 | A(9-12-14) | 119.4 | | | | |
| R(21-25) | 1.4 | A(9-12-17) | 118.4 | | | | |
| R(21-26) | 1.08 | A(14-10-15) | 121 | | | | |
| R(23-25) | 1.4 | A(10-14-12) | 120.6 | | | | |
| R(23-27) | 1.08 | A(10-14-16) | 118.9 | | | | |

## IV.VIBRATIONAL ANALYSIS:
## CH STRETCHING:

The CH stretching vibrations are characteristic vibrations of molecules in which aromatic compounds are present. In case of title molecule, these vibrations have been observed at 3108 and 3050 cm$^{-1}$[11] and the calculated values falls in the range 3176-3068 cm$^{-1}$, which are in good agreement with observed and reported values[5]. The individual peak for CH stretch on thiazole part has not been observed separately but the calculated vibrational mode is present at 3176Cm$^{-1}$ which in good agreement with the reported values.

**Table 2: Calculated and observed vibrational frequencies (cm$^{-1}$) and assignments with potential energy distribution (PED) of CL-PPT.**

| ModeNo. | Calculated unscaled | scaled | Experimental IR | Assignment(%PED) |
|---|---|---|---|---|
| 5 | 3204 | 3108 | 3108 | ν-ph-CH |
| 10 | 3163 | 3068 | 3050 | ν-ph-CH |
| 11 | 1640 | 1590 | 1594 | ν-ph-C=C |
| 16 | 1551 | 1504 | 1504 | ν-C$_2$=C$_3$(72)+ν-C$_2$-C$_7$(25 |
| 17 | 1525 | 1479 | 1469 | β-CH(45)+ν-C$_1$=N$_6$(30) |
| 19 | 1489 | 1445 | 1436 | βCH(78)+ν-ph-C=C(10) |
| 20 | 1460 | 1416 | 1395 | β-CH(55)+ν-ph-C=C(45) |
| 22 | 1356 | 1316 | 1311 | β-CH(65) |
| 23 | 1338 | 1298 | | ν-ph-C=C(63)+βCH(40) |
| 24 | 1325 | 1285 | 1282 | ν-phC=C(63)+βCH(40) |
| 26 | 1255 | 1217 | 1233 | ν-C$_{18}$-C$_1$(35)+βCH(25) |
| 27 | 1229 | 1192 | 1198 | β-CH(40)+βC$_3$H$_5$(59) |
| 31 | 1125 | 1091 | 1101 | βCH(81) |
| 32 | 1117 | 1083 | | βCH(51) |
| 33 | 1097 | 1064 | 1049 | βCH(35)+βC$_3$H$_5$(25) |
| 36 | 1032 | 1001 | 1001 | γCH(58) |
| 40 | 1016 | 986 | 973 | γCH(65) |
| 44 | 926 | 898 | 896 | γCH(90) |
| 45 | 905 | 878 | | δ -thiazolering(48) |
| 46 | 877 | 851 | 827 | γCH(65) |
| 49 | 805 | 781 | 764 | ν-S$_4$-C$_3$(65)+δ-ring-dia(22) |
| 50 | 770 | 747 | 719 | γC$_3$-H$_5$(65)+γCH(15) |
| 53 | 712 | 691 | 686 | γC$_3$-H$_5$(70)+γCH(23) |
| 58 | 618 | 600 | 593 | δ-molecule (35) |
| 60 | 543 | 527 | 491 | β-molecule(45) |
| 64 | 423 | 410 | 418 | β-ring(25) |

ν: stretching; νas: asymmetric stretching; νs: symmetric stretching; ϒ: out-of-plane bending; β: in-plane bending; τ: torrion; δ: deformation; ω: wagging; ζ: twist; r: rock: s: scissor; *: thiazole group.

### C=C stretching and CH bending vibrations:

In case of CL-PPT the ν-C=C vibrations have been observed at 1594,1504 and 1282Cm$^{-1}$ vibrational modes(ref ). According to literature these vibrations occurs in the region 1500 to 1680Cm$^{-1}$ [12]. The calculated values for these vibrations are in the range of 1590-1504 cm$^{-1}$.The β-CH vibrational modes have been observed at 1436, 1395, 1311, 1198, 1049 and 1049 cm$^{-1}$[5]on thiazole part of the molecule and the calculated values occur in the region 1479-1034Cm$^{-1}$ which is in good agreement with the observed and reported values(ref).The calculated values of γ- CH vibrational modes occurs in the range 1001-691cm-1 which are in good agreement with the observed vibrational modes which occurs at 1001, 973, 896, 827, 719 and 686 cm$^{-1}$[5] and reported values.

### Other vibrations:

The Other vibrations namely ring deformation, ring bending, molecule deformations have been observed at 593, 491and 418cm$^{-1}$. The calculated values for these vibrations are in good agreement with the reported and observed values [13]. The ν-S$_4$-C$_3$ vibrations have been observed at 719Cm$^{-1}$ and the calculated value for this occurs at 781cm$^{-1}$, which is in good agreement with the observed and reported value [5].
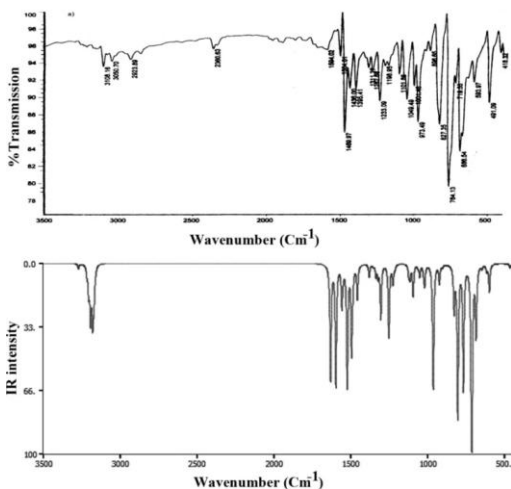
*Fig. 2:- IR spectra of CL-PPT: (a) experimental FT-IR spectra[10] in KBr and (b) calculated spectra obtained from B3LYP/6- 311+G level theory.*

## V. THERMAL PROPERTIES

The study of thermodynamic properties of organic molecules has its own importance in the research area. The Thermodynamic properties like total energy ($E_{tot}$), heat capacities ($C_V$) entropy ($S$) and total thermal energy ($\epsilon_{tot}$), rotational constants ($r_C$) and rotational temperatures ($r_T$) of CL-PPT have been calculated at constant pressure using the B3LYP/6-311+G optimized geometries and the results are tabulated in Table 3. Various thermodynamic properties have been calculated at different temperatures using the B3LYP/6-311+G optimized geometry and the results are tabulated in Table 4. It can be seen from the Table 4, that the thermodynamic function value increases with increasing the temperature and this may be attributed to the fact that the intensities of molecular vibration increases as the temperature increases [14]. The correlations between these thermodynamic properties and temperature are shown in Fig. 3.The empirical correlations between the thermodynamicproperties and temperature are deduced as follows:

$$H = 7 \times 10^{-5}T^2 + 0.017T + 248.9$$
$$C_V = -8 \times 10^{-5}T^2 + 0.3296 + 0.501$$
$$E_{tot} = 6 \times 10^{-5}T^2 - 0.21T + 099.7$$
$$S = 0.205T + 61.83$$

All the above-mentioned thermodynamic data may be useful in the field of thermodynamics, for further study on the title molecule.
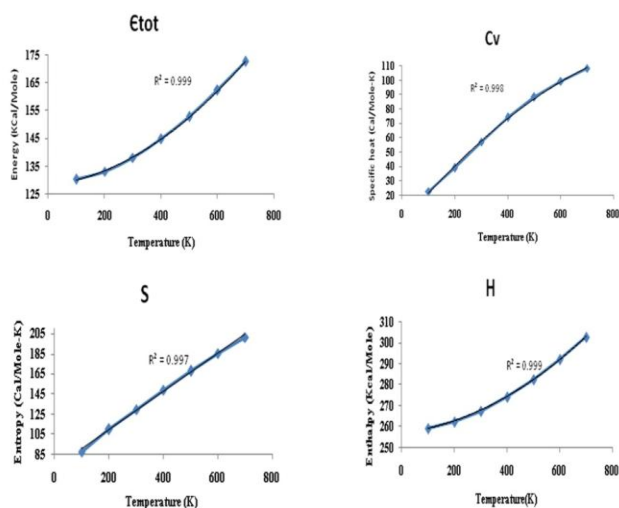


*Fig. 3: Correlation graph between Temperature and Thermodynamic properties of CL-PPT*

*Table 3: Thermodynamic properties of CL-PPTat different temperatures at B3LYP/6-311+G level*

| T | $\epsilon_{tot}$ | $C_v$ | S | H |
|---|---|---|---|---|
| 100 | 133.9 | 23.6 | 83.1 | 248.7 |
| 200 | 136.7 | 33.7 | 105.4 | 257.4 |
| 300 | 142.6 | 56.4 | 126.6 | 260.9 |
| 400 | 149.4 | 70.6 | 143.8 | 263.5 |
| 500 | 156.6 | 86.7 | 160.5 | 275.4 |
| 600 | 168.8 | 95.9 | 179.7 | 289.9 |
| 700 | 178.6 | 102.8 | 195.8 | 295.5 |

## VI. NLO PROPERTIES

In case of CL-PPT the non-linear optical properties like total dipole moment ($\mu_{tot}$), mean polarizability ($\alpha_m$), molecular first hyperpolarizability ($\beta_\mu$), and total hyperpolarizability ($\beta_{tot}$) have been calculated using B3LYP/6-311+G optimized geometries. The values of all these properties have been calculated using standard equations available in literature[15]. The calculated dipole moment, mean linear polarizability, first hyperpolarizability and total polarizability values of **CL-PPT** listed in Table 5(1.17 Debye, 32.29 x $10^{-24}$ esu, 2.08 x $10^{-30}$ esu, 2.9 x $10^{-30}$ esu.

***Table 4: The dipole moment (in Debye), polarizability (in esu), hyperpolarizabilities (in esu) tensors computed with the B3LYP/6-311+G method.***

| | | | |
|---|---|---|---|
| $\mu_x$ | -0.063 | $\beta_{xxx}$ | 95.07 |
| $\mu_y$ | -0.29 | $\beta_{xxy}$ | 75.93 |
| $\mu_z$ | -1.13 | $\beta_{xyy}$ | 38.53 |
| $\mu_{tot}$ | **1.17** | $\beta_{yyy}$ | -3.41 |
| | | $\beta_{xxz}$ | 126.02 |
| $\alpha_{xx}$ | 207.69 | $\beta_{xyz}$ | -25.43 |
| $\alpha_{xy}$ | 42.32 | $\beta_{yyz}$ | -55.67 |
| $\alpha_{yy}$ | 144.79 | $\beta_{xzz}$ | -310.68 |
| $\alpha_{xz}$ | -22.39 | $\beta_{yzz}$ | -73.73 |
| $\alpha_{yz}$ | 61.1 | $\beta_{zzz}$ | 207.67 |
| $\alpha_{zz}$ | 343.1 | $\beta_\mu$ | $1.28 \times 10^{-30}$ |
| $\alpha_m$ | $32.29 \times 10^{-24}$ | $\beta_{tot}$ | $2.9 \times 10^{-30}$ |

T in Kelvin; $\text{E}_{tot}$ in Kcal/mol; Cv in cal/mol-K; S in Cal/mol-K; H in K cal/mol

### VII. HOMO-LUMO ENERGY GAP ($\Delta$ E)

The frontier molecular orbitals namely highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO) and their properties such as energy are very useful for physicists and chemists for evaluating the charge transfer within the molecule. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties [16]. The energy gap between HOMO and LUMO explains the biological activity of the molecule, which is due to the change in partial charge and to the change in total dipole moment. The plots of HOMO, LUMOs and $\Delta$ E are shown in Fig. 5.
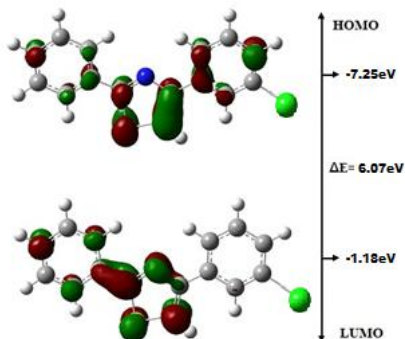


*Fig 4 - Frontier molecular orbitals (HOMO and LUMO) and the energy gap ($\Delta$ E) of CL-PPT*

The HOMO and LUMO energy calculated by B3LYP/6-311+G method in gas phase is given below.
HOMO energy (B3LYP) = -7.25eV
LUMO energy (B3LYP) = -1.18eV
HOMO–LUMO energy gap (B3LYP) = 6.07eV

### VIII. CONCLUSIONS

In the present study, the structural geometrical parameters, vibrational frequencies, thermodynamic and nonlinear optical properties of **CL-PPT** have been studied using B3LYP method with 6-311+G basis set. The structural parameters like bond length and angles obtained are in good agreement with reported values of thiazoles. It can be seen that the calculated vibrational frequencies of **CL-PPT** computed using DFT/B3LYP/6-311+G method are in good agreement with the experiment. The spectral frequencies have been calculated using above-mentioned methodare compared with the observed spectra. The complete vibrational assignments of wavenumbers have been made on the basis of potential energy distribution and found to be in good agreement with the experiment. The thermodynamic properties have been calculated for the title molecule may be helpful in the estimation of chemical reaction directions. Using the B3LYP/6-311+G optimized geometry, the thermodynamic properties are calculated at constant pressure by varying the temperature and the correlation between them is found to be linear. The polarizability, first hyperpolarizability and total hyperpolarizability imply that the title molecule may be useful as a NLO material. Furthermore, from the molecular orbital analysis, it can be seen that there is a possibility of intermolecular charge transfer within the molecule. From these studies, it can be concluded that the theoretical methods are useful in predicting the geometrical, vibrational, optical, thermodynamic and charge transfer properties for the new molecule in advance.

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