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# DFT COMPUTATIONS AND SPECTROSCOPIC ANALYSIS OF 2-CYCLOPENTYL-4-CHLOROPHENOL

**C. Cynitha Wise Bell [1] and D. Arul Dhas [2]**
*[1]Research Scholar, [2]Assistant Professor,*
*[1,2]Department of Physics, Physics Research Centre,*
*[1,2]Nesamony Memorial Christian College,Marthandam,India*
*cyniwise@gmail.com[1], aruldhas_2k4@gmail.com[2]*

***Abstract:*** *Spectroscopic studies and theoretical quantum chemical calculations of 2-cyclopentyl-4-chlorophenol have been carried out by density functional theory method. The equillibrium geometry, various bonding features and harmonic vibrational wavenumber of 2-cyclopentyl-4-chlorophenol have been computed by B3LYP method. The calculated molecular geometry has been compared with the experimental data. The various intramolecular interactions has been exposed by natural bond orbital analysis (NBO). Mulliken population analysis was performed on the atomic charges and HOMO-LUMO energies were also calculated.*

***Key words****: Charge analysis , DFT, HOMO-LUMO, ICT, NBO,*

## I. Introduction

2-cyclopentyl-4-chlorophenol is a antihypertensive drug. It is used to prevent the complications of high blood pressure, such as stroke and myocardial infarction[1]. Phenol derivatives are interesting molecules for theoretical studies due to their relatively small size and similarity to biological species [2]. Spectral and vibrational analysis have been carried out using computation and experimental methods. Intramolecular hydrogen bonding interaction have received much attention from both practical and theoretical values, as they can determine the structure and activities of biological molecules. Vibrational spectroscopic investigation with the help of quantum chemical computation have recently be used as an efficient tool in the structural analysis of cardiovascular compounds, DFT with the B3LYP method using Gaussian '09 program package is used for calculation. Hence, the present investigations aim to interpret the vibrational characteristics of 2-cyclopentyl-4-chlorophenol were studied using their FT-IR, FT-Raman, HOMO-LUMO energies and NBO analysis.

## II. Experimental details

2-cyclopentyl-4-chlorophenol was purchased from Sigma–Aldrich (St. Louis, MO, USA) and used without further purification. The IR spectrum of each sample was recorded using a PerkinElmer Spectrum One FTIR spectrometer in the region 400–4000 $cm^{-1}$, using a KBr sample pellet. The resolution of the spectrum was 4 $cm^{-1.}$ An FT-Raman spectrum in the range 50–3500 $cm^{-1}$ was also recorded using a powdered sample, with the 1064 nm line provided by an Nd:YAG laser employed as the excitation source, and analyzed on Bruker Vertex 70 FT-IR-RAM-II FT-Raman module.

## III. Computation

The DFT computations for the 2-cyclopentyl-4-chlorophenol was carried out in the Gaussian 09 program package using "ultrafine" integration grids. The calculations were performed at the B3LYP level with the standard 6-311 G(d,p) basis set in order to derive the optimized geometry, vibrational wavenumbers and natural bond orbital analysis of 2-cyclopentyl-4-chlorophenol.

## IV. Result and Discussion

### 4.1 Optimized geometry

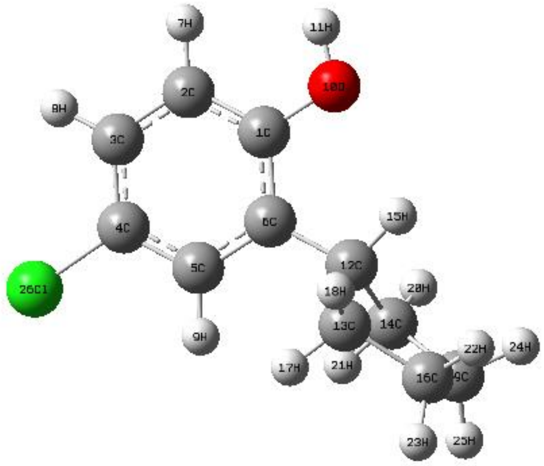


**Fig. 1 Structure of 2-cyclopentyl-4-chlorophenol**

The calculated data of 2-cyclopentyl-4-chlorophenol are in close agreement with the experimental values [Table1]. The bond length $C_1$-$C_6$ is increased by 1.4057Å. This is because of the presence of cyclopentyl ring. The $C_1$-$O_{10}$ bond length is 1.3702Å and its experimental value is 1.378Å. This shows that the lone pair of electrons over oxygen atom is involved in the conjugation with the π-electrons of the ring [3]. The bond angle $C_3$-$C_4$-$C_5$ (120.9°) of carbon atom attached to the chlorine atom exceeds the normal value 120°. This is due to the electron donating nature of chlorine atom [4]. The bond angle $C_1$-$C_5$-$C_6$ (117.6°) at the substitution approximately equal as well as slightly lower than the benzene ring cyclopentyl ring moiety is essentially out-of-plane with benzene ring as evident from torsional angles $C_5$-$C_6$-$C_{12}$-$C_{13}$ = -59.4 ° and $C_1$-$C_6$-$C_{12}$-$C_{14}$ = -120.3 °.

**Table 1: Selected optimized parameters of 2-cyclopentyl-4-chlorophenol**

| **Parameter** | **Bondlength** | **XRD(e)** |
|---|---|---|
| $C_1$-$O_{10}$ | 1.370 | 1.378 |
| $C_1$-$C_6$ | 1.405 | 1.405 |
| $C_3$-$C_4$-$C_5$ | 120.9 | 124.0 |
| $C_1$-$C_5$-$C_6$ | 117.6 | 119.6 |
| $C_1$-$C_6$-$C_{12}$-$C_{13}$ | -120.3 | 165.0 |
| $C_5$-$C_6$-$C_{12}$-$C_{13}$ | -59.4 | -43.80 |

### 4.2 Vibrational analysis

The C-H stretching vibrations normally lies between 3100 and 3000cm$^{-1}$. In this region the bands are not affected appreciably by the nature of substituents. The C-H symmetric stretching is observed as strong band in FT-IR at 3092 cm$^{-1}$.The C-C stretching modes of the phenyl group are expected in the range from 1650 to 1200cm$^{-1}$. In the present work C-C stretching observed at 1588 cm$^{-1}$ in FT-IR spectrum. The O-H stretching absorption in the region 3620-3590 cm$^{-1}$. FT-IR spectrum shows an absorption position at 3715 cm$^{-1}$[5].

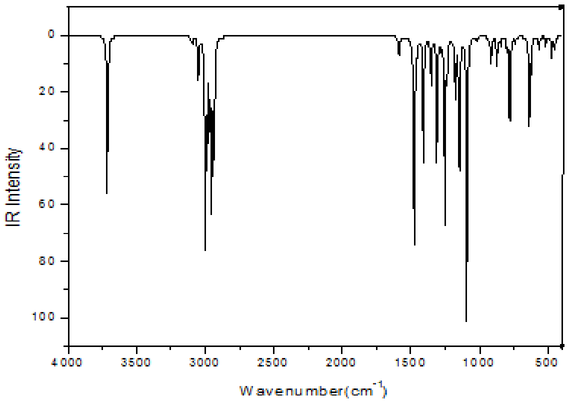


**Fig. 2 FT-Raman Spectrum for 2-cyclopentyl-4-chlorophenol**

### 4.3 NBO analysis

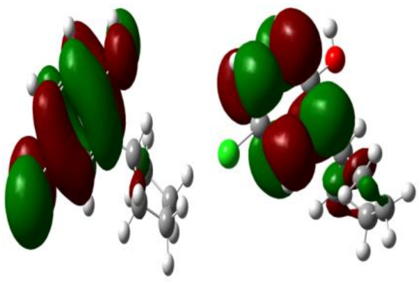
The interaction of σ($O_{10}$–$H_{11}$) distribute to σ*($C_1$–$C_6$) which leads to stabilization energy of 18.4 KJmol$^{-1}$. The interaction of σ($C_6$–$C_{12}$)→σ*($C_{12}$–$H_{15}$) leading to low stabilization energy of 2.7 KJmol$^{-1}$. In NBO analysis, the strong intramolecular hyperconjugation interaction of ($C_1$-$C_2$) from $O_{10}$ of n($O_{10}$) →π*($C_1$-$C_2$) which increases ED that weakens the respective bonds $C_3$-$C_4$ leading to stabilization of 24.09 KJmol$^{-1}$ [6]. The interaction between the lonepair Cl with antibonding $C_4$-$C_5$ results into the stabilization of 6.8 KJmol$^{-1}$.

**Table 2: NBO analysis for 2-cyclopentyl-4-chlorophenol**

| Donor NBO(i) | ED(i) (e) | Acceptor NBO(j) | ED(j) (e) | $E^{(2)}$ (kj/mol) |
|---|---|---|---|---|
| σ($O_{10}$–$H_{11}$) | 1.9883 | σ*($C_1$–$C_6$) | 0.03352 | 18.4 |
| σ ($C_6$–$O_{12}$) | 1.9661 | σ*($C_{12}$–$H_{15}$) | 0.02223 | 2.7 |
| LP(1) $O_{10}$ | 1.9794 | σ*($C_1$-$C_2$) | 0.02617 | 24.09 |
| LP(1) $Cl_{26}$ | 1.9922 | σ*($C_4$-$C_5$) | 0.02820 | 6.8 |

### 4.4 HOMO-LUMO analysis

Spatial distribution of molecular orbitals especially those of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are excellent indicators of electron transport in molecular system. The charge transfer concentrates on the phenol group. The HOMO-LUMO energy gap is -0.13025 eV. The low value of the HOMO-LUMO energy gap confirms charge transfer within the molecule.



HOMO LUMO

**Fig. 3 HOMO and LUMO plots for 2-cyclopentyl-4-chlorophenol**

### V. Conclusion

The optimized geometries of 2-cyclopentyl-4-chlorophenol were determined and analyzed at the DFT level. The DFT calculated values of the vibrational wavenumbers were agreed well with the experimental datas. The NBO analysis reveals hyperconjugative interaction, ICT and stabilization of molecules. The low HOMO–LUMO energy gap clearly reveals the structure activity relation of the molecule.

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