

# SPECTROSCOPIC ANALYSIS AND CHARGE TRANSFER INTERACTION STUDIES OF N-(4-CHLOROPHENYL)-2,2- DIPHENYLACETAMIDE

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**ABSTRACT:** *The Density functional theory (DFT) and vibrational analysis of n-(4-chlorophenyl)-2,2-diphenylacetamide herbicide has been carried out using FT-IR spectroscopic technique and compared with computational technique. The FT-IR spectra have been recorded in the region 400–4000 cm<sup>-1</sup>. The geometry has been optimized at B3LYP level of theories with 6-311G(d,p) basis set using Gaussian '09 program package. The NBO analysis showed the intramolecular N-H...O and C-H...O hydrogen bonds in the crystal structure of n-(4-chlorophenyl)-2,2-diphenylacetamide. The calculated geometrical parameters also show a very strong hydrogen bond. The Mulliken population analysis on atomic charges and the HOMO-LUMO energy were also calculated.*

**Keywords:** *DFT, FT-IR, Herbicide, HOMO-LUMO, NBO.*

## I. INTRODUCTION

Herbicides are commonly known as weed killers, which are used to kill unwanted plants [1]. N-(4-chlorophenyl)-2,2-diphenylacetamide as a pre-emergent herbicide is widely employed for control of annual grasses and broad leaf weeds in tomato, potato, peanut and soybean plants (Schultz and Tweedy, 1972 and Sirons et al, 1981). The present work reports a study on n-(4-chlorophenyl)-2,2-diphenylacetamide using spectroscopic techniques. The natural bond orbital (NBO) analysis has been carried out to interpret hyperconjugative interaction and intramolecular charge transfer (ICT) [2]. The calculated value of HOMO-LUMO energy gap is used to interpret the biological activity of the molecule. Intramolecular hydrogen bonding interactions have received much attention from both practical and theoretical perspectives as they can determine the structures and activities of biological molecule. The optimized structure of n-(4-chlorophenyl)-2,2-diphenylacetamide is given in Fig.1.

## II. EXPERIMENTAL DETAILS

N-(4-chlorophenyl)-2,2-diphenylacetamide 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<sup>-1</sup>, using a KBr sample pellet. The resolution of the spectrum was 4 cm<sup>-1</sup>. An FT-Raman spectrum in the range 50–3500 cm<sup>-1</sup> 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.

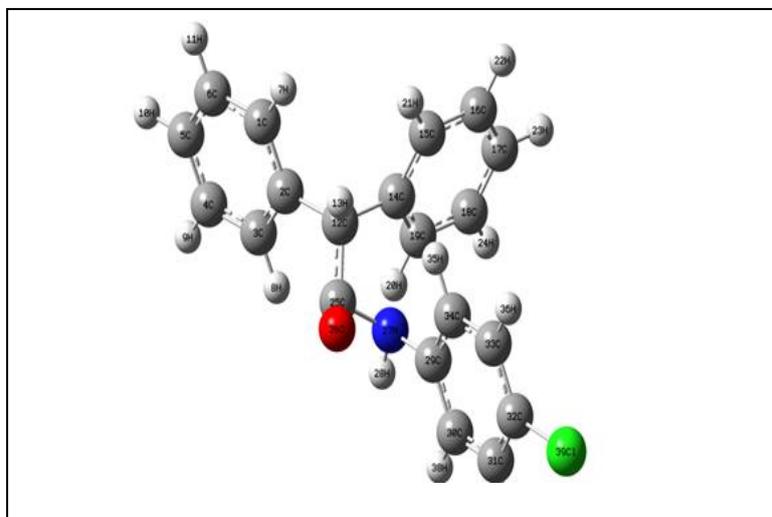
## III. COMPUTATIONAL DETAILS

The DFT computations of n-(4-chlorophenyl)-2,2-diphenylacetamide has been performed using Gaussian 09 program package [3] at the B3LYP level with standard 6-311G (d,p) basis set. This has been successfully applied in order to derive the optimized geometry and vibrational wave number of the normal modes.

## 4. RESULT AND ANALYSIS

### 4.1 OPTIMIZED GEOMETRY

**Fig.1 Optimized structure of N-(4-chlorophenyl)-2,2-diphenylacetamide**



The optimized geometry parameters of n-(4-chlorophenyl)-2,2-diphenylacetamide at DFT level of computations are listed in Table.1. The small deviations are probably due to the intramolecular interactions of the molecule.

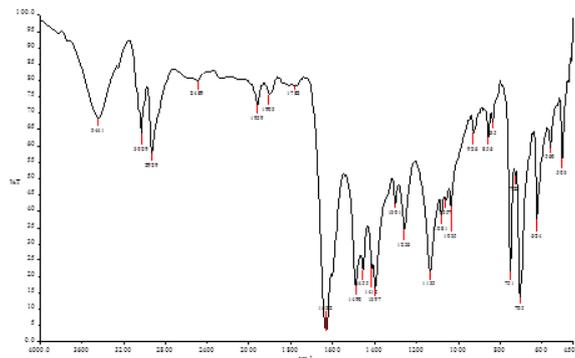
**Table:1**

Optimized bond length and bond angle					
Bond Length / (Å)			Bond Angle / (°)		
Experi mental Value	n-(4-chlorophenyl)- 2,2-diphenyl acetamide	Calcula ted Value	Experimental Value	n-(4-chlorophenyl)- 2,2-diphenyl acetamide	Calcula ted Value
1.397	C <sub>1</sub> -C <sub>2</sub>	1.399	120.3	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	120.3
1.527	C <sub>2</sub> -C <sub>12</sub>	1.524	119.6	C <sub>3</sub> -C <sub>4</sub> -H <sub>9</sub>	120.1
1.085	C <sub>1</sub> -H <sub>7</sub>	0.949	124.5	O <sub>26</sub> -C <sub>25</sub> -N <sub>27</sub>	123.9
1.374	C <sub>25</sub> -N <sub>27</sub>	1.331	102.6	C <sub>12</sub> -H <sub>13</sub> -C <sub>25</sub>	106.8
1.215	C <sub>25</sub> -O <sub>26</sub>	1.229	120.4	C <sub>12</sub> -O <sub>26</sub> -C <sub>25</sub>	122.3

The optimized parameters of n-(4-chlorophenyl)-2,2-diphenylacetamide shows that there are some changes observed in C- H bond length due to variation in the charge distribution on the carbon atom of the benzene ring. The significant change identified in C-C bond length C<sub>1</sub>-C<sub>2</sub>(0.002Å) is smaller when compared with C<sub>2</sub>-C<sub>12</sub>(0.003Å) indicates an extension of conjugation in the aromatic ring of n-(4-chlorophenyl)-2,2-diphenylacetamide to oxygen. Due to hydrogen bonding the C=O bond length increases by 0.014(Å). The reduction in the bond angle in O<sub>26</sub>-C<sub>25</sub>-N<sub>27</sub> is (0.6°) (Table.1)

#### 4.2 VIBRATIONAL ANALYSIS

The amino groups are generally considered as electron-donating substituents in aromatic ring systems[4]. Generally N-H group share its lonepair of electron with the  $\sigma$  electrons in the ring. The H bonding leads to a reduction in NH stretching wavenumber and an increase in IR intensity[5]. For secondary amines, it is known that symmetric NH stretching will give rise to a band in the range  $3500-3310\text{cm}^{-1}$ [6].



In n-(4-chlorophenyl)-2,2-diphenylacetamide, the stabilization energy contributions from the  $\sigma(\text{C}_{12}-\text{C}_{25}) \rightarrow \sigma^*(\text{N}_{27}-\text{C}_{29})$  interactions are  $4.71 \text{ kJmol}^{-1}$  [Table:2]. The stabilization energy contributions from the  $\sigma(\text{H}_{28}-\text{N}_{27}) \rightarrow \sigma^*(\text{C}_{25}-\text{O}_{26})$  interactions are  $4.20 \text{ kJmol}^{-1}$ . A large number of stabilizing orbital interactions are observed in acceptor [11]. The strong intramolecular H-bonding explains the stability of the n-(4-chlorophenyl)-2,2-diphenylacetamide and increased the herbicidal activities of these compounds.

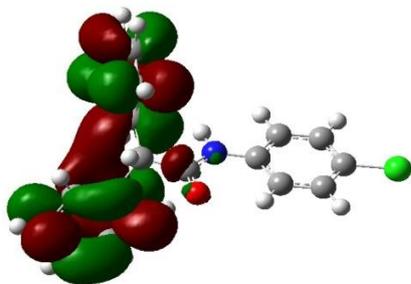
**Table:3**

Possible hydrogen bonding of n-(4-chlorophenyl)-2,2-diphenylacetamide										
Compound	DONOR		ACCEPTOR		$E^{(2)}/\text{KJmol}^{-1}$	H.O	D-H(Å)	H-A(Å)	D-A(Å)	D-H...A( $^\circ$ )
	NBO(i)	E.D/e	NBO(j)	E.D/e						
n-(4-chlorophenyl)-2,2-diphenylacetamide		1.859		0.009						104.7
	O <sub>26</sub>	-0.241	$\sigma^*(\text{N}_{27}-\text{H}_{28})$	0.425	0.72	SP <sup>1</sup>	1.086	2.246	2.731	

#### 4.4 HOMO-LUMO ENERGY GAP

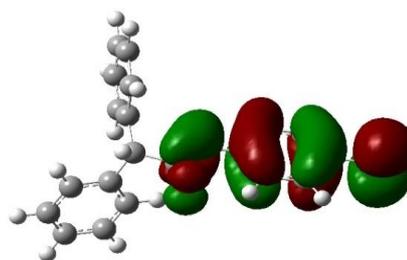
In the frontier region, neighbouring orbitals are being often closely spaced. In such cases, consideration of only the HOMO and LUMO may not yield a realistic description of the frontier orbitals. The HOMO-LUMO energy gap of title compound as calculated at the B3LYP/6-311G(d,p) level, which reveals that the energy gap reflects the chemical activity of the molecule. The LUMO as an electron acceptor represents the ability to obtain an electron, and HOMO presents the ability to donate an electron. The energy gap is  $0.13179 \text{ eV}$ . The energy gap of HOMO-LUMO explains the eventual charge transfer interaction within the molecule, which influences the biological activity of the molecule. Consequently, the lowering of the HOMO-LUMO band gap is essentially a consequence of the large stabilization of the LUMO due to the strong electron accepting ability of the electron acceptor group [12]. The HOMO-LUMO energy separation can be used as a sign of kinetic stability [13].

#### LUMO



$$\Delta E = 0.13841 \text{ eV}$$

#### HOMO



#### V. CONCLUSION

In the present work, complete vibrational analysis has been made for proper frequency contributions of n-(4-chlorophenyl)-2,2-diphenylacetamide. The FT-IR frequencies of the title compound have been theoretically computed using DFT methods. The optimized parameters have also been determined and compared with experimental data. From the optimized parameters, it was concluded that due to hydrogen bonding, the C=O bond length increases. NBO result reflects the charge transfer within the molecule. NBO analysis reveals that the redshifting of the N-H stretching wave number exhibits the decrease in N-H bond order values that occurs due to donor-acceptor interactions. This leads to the stability and increase in herbicidal activity of n-(4-chlorophenyl)-2,2-diphenylacetamide. Due to intra molecular C-H...N and N-H...Cl hydrogen bonding there is an increase in the electron density of the antibonding orbital of the N-H bond, electron density delocalization, decrease in the N-H distance, and an increase in the vibrational stretching wavenumber. The lowering of the HOMO-LUMO energy gap value has substantial influence on the intramolecular charge transfer and bioactivity of the molecule.

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