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SPECTROSCOPIC ANALYSIS AND CHARGE TRANSFER INTERACTION STUDIES OF N-(3,4- DIFLUROPHENYL)-2,2-DIPHENYL ACETAMIDE

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Abstract-Extensive spectroscopic investigations along with theoretical quantum chemical studies on N- (3,4 – diflurophenyl)-2,2 diphenyl acetamide have been consummated. The fundamental vibrational transitions were addressed by experimental FTIR(4000-400cm-1) and FT-Raman (3500-50 cm-1) techniques. The HOMO-LUMO analysis is used to determine the Charge transfer within the molecule. Stability of the molecule arising from hyperconjugative interactions and charge delocalization has been analyzed using natural bond orbital (NBO) analysis . NBO showed that the intramolecular N-H…F and C-H…O hydrogen bond in this crystal structure. The structural and spectroscopic data of the molecule were calculated by using density functional theory (DFT) employing B3LYP methods with the 6-311G(D,P) basis set. The geometry of the molecule was fully optimized. As a result, the optimized geometry and calculated spectroscopic data show a good agreement with the experimental result.

Keywords – FT-IR, FT-Raman, DFT, HOMO-LUMO, NBO.

I. INTRODUCTION

Herbicides are commonly known as weed killers, which are used to kill unwanted plants [1]. N-(3,4-diflurophenyl)-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. The present work reports a study on n-(3,4-diflurophenyl)-2,2-diphenylacetamide using spectroscopic techniques and also encompasses the possibility of hydrogen bonding . 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-(3,4-diflurophenyl)-2,2-diphenylacetamide is given in Fig.1.

II. EXPERIMENTAL DETAILS

The compound N-(3,4-diflurophenyl)-2,2-diphenylacetamide in solid state 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}, which was calibrated using a KBr sample pellet. The spectral resolution of the spectrum was 4.0 cm^{-1}.

III. COMPUTATION

The first task for the computational work was to determine the optimized geometry of the compound. The DFT computations of n-(3,4-diflurophenyl)-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.

IV. RESULT AND DISCUSSION

A. Optimized geometry

The optimized geometry parameters of n-(3,4-diflurophenyl)-2,2-diphenylacetamide at DFT level of computations are listed in Table1. The small deviations are probably due to the intramolecular interactions of the molecule.

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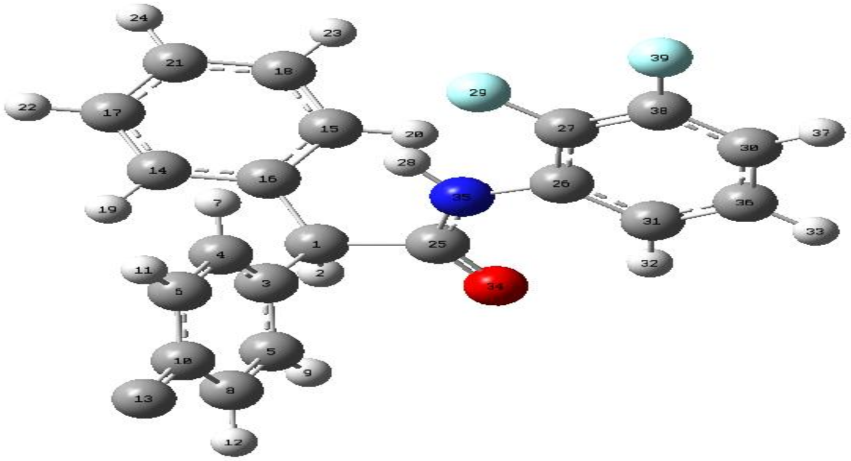


Fig 1. Optimized structure of N-(3,4-diflurophenyl)-2,2-diphenylacetamide

Table 1: Selected optimized parameters of N-(3,4-diflurophenyl)-2,2-diphenylacetamide

Parameters	Bondlength and Bond angle	
	Experimental	Calculated
$C_2 – C_{12}$	1.527 Å	1.524 Å
$C_1–H_7$	1.085 Å	0.949 Å
$C_{25}– N_{27}$	1.374 Å	1.331 Å
$C_{25}– O_{26}$	1.215 Å	1.229 Å
$C_3–C_5–H_9$	$119.4\ ^0$	118.9^0
$C_1–C_{25}– O_{34}$	$122.3\ ^0$	119.16^0
$O_{34}–C_{25}– N_{35}$	$125.6\ ^0$	126.6^0
$C_{27}–F_{29}– C_{38}$	$120.4\ ^0$	120.3^0

The optimized parameters of n-(3,4-diflurophenyl)-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. Worth mentioning differences are observed in C-N bondlength. The calculated lengths are bigger than experimental values. This enhancement could be due to the presence of the oxygen atom near the ring and amide group. The significant change identified in C-C bond length C_1-C_2 (0.002Å) is smaller when compared with C_2-C_{12} (0.003**Å)** indicates an extension of conjucation in the aromatic ring of n-(3,4-diflurophenyl)-2,2-diphenylacetamide to oxygen. Due to hydrogen bonding the C=O bond length increases by 0.014**(**Å). The bond angle $O_{34}–C_{25}– N_{35}$ is decreased from the experimental value (125.6 and 126.6˚ for exp. and cal., respectively). This clearly shows that due to the prescence of electronegative oxygen atom (O_{34}). Also for $C_1–C_{25}– O_{34}$ bond angle is bigger than experimental values, this can be due to the presence of oxygen atom in our title molecule. Therefore some bond angles near the oxygen atom are different experimental values.

B. VIBRATIONAL ANALYSIS

The molecule of N-(3,4-diflurophenyl)-2,2-diphenylacetamide consists of 39 atoms, so, it has 111 normal vibrational modes. 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 σ electrons in the ring. The H bonding leads to a reduction in NH stretching wavenumber and an increase in IR intensity[5].

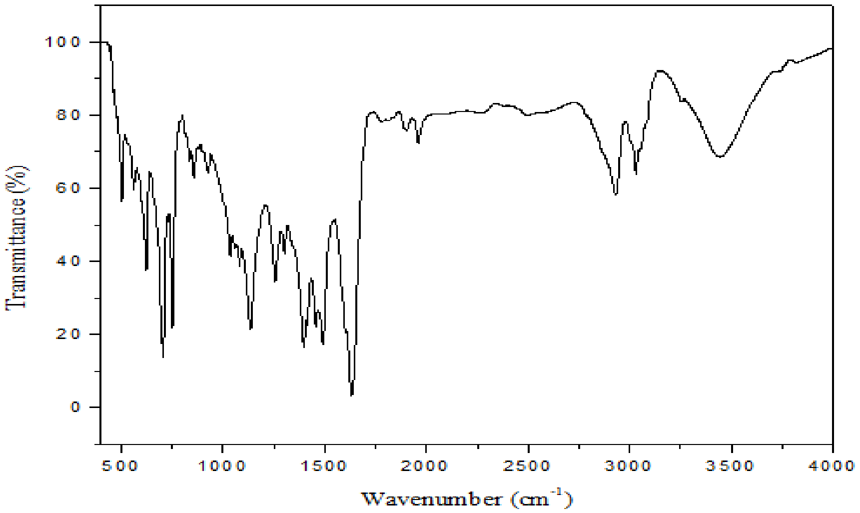


Fig 2. FT-IR Spectrum of N-(3,4-diflurophenyl)-2,2-diphenylacetamide

The IR spectrum shows a strong band at1632cm^{-1} corresponds to the C=O Stretching vibration. The C=C Stretching mode of the benzene ring in the IR Spectrum is due to the charge transfer interaction between donor and acceptor groups. The CH_2 Symmetric Stretching vibrations are observed at 3029cm^{-1} as very weak band in FT-IR Spectrum.

For primary amines, the asymmetric NH_2 stretching will give rise to a band in the range 3500- 3420 cm^{-1} , while symmetric stretching will appear between 3420 -3280 cm^{-1}(6). In n-(3,4-diflurophenyl)-2,2-diphenylacetamide the symmetric CH stretching calculation values are 3163 cm^{-1} with a PED of (100%).

C. NBO ANALYSIS

NBO analysis provides a description of the structure of a compound based on a set of localized bond, and antibond that can be used to identify and confirm possible intra and intermolecular interactions between the units that would lead to proper and improper hydrogen bonding. The second order perturbation theory analysis of Fock matrix was carried out to evaluate the donor-acceptor interactions in the NBO analysis [7]. NBO of n-(3,4-diflurophenyl)-2,2-diphenylacetamide shows strong intramolecular hyperconjucative interaction. The system is also stabilized due to the interactions between the pie type orbital containing lone pairs of electron of n(O_{34}) with antibonding (**C_{31}-H_{32}**) **σ(C_{31}-H_{32})** orbitals respectively resulting in the stabilization of carbonyl structure due to the resonance delocalization. These interactions are observed as increase in electron density(ED) in C-C, C-N antibonding orbital that weakens the respective bonds[8]. The weakening and elongation of N-H bonds occur due to hydrogen bonding.

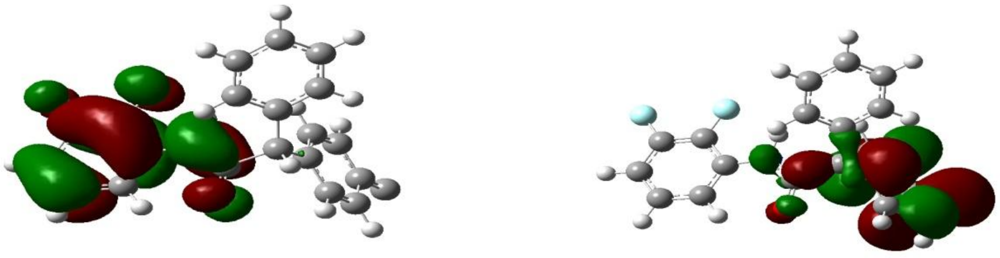
Table 2: NBO analysis for N-(3,4-diflurophenyl)-2,2-diphenylacetamide

Second order perturbation theory					
COMPOUND	DONOR NBO(i)	E.D/e	ACCEPTOR NBO(j)	E.D/e	$E^{(2)}$/kJmol^{-1}
n-(3,4-diflurophenyl)-2,2-diphenylacetamide	$\sigma(C_1-C_{25})$	1.903 -0.728	$\sigma^*(C_{26}-N_{35})$	0.031 0.275	19.75
	$\sigma(C_{12}-C_{25})$	1.961 -0.619	$\sigma^*(N_{35}-C_{29})$	0.032 0.410	19.70
	$\sigma(H_{28}-N_{35})$	1.982 -0.666	$\sigma^*(C_{25}-O_{34})$	0.013 0.599	17.57
	$\sigma(C_1-H_2)$	1.948 -0.6378	$\sigma^*(C_3-C_4)$	0.028 0.349	19.91

In n-(3,4-diflurophenyl)-2,2-diphenylacetamide**,** the stabilization energy contributions from the σ(C_{12}-C_{25}) → **σ***(N_{35}-C_{29}) interactions are 19.70. kJmol^{-1}[Table:2]. The stabilization energy contributions from the σ**(**H_{28}-N_{27}) → σ*(C_{25}-O_{34})interactions are 17.57 kJmol^{-1}. A large number of stabilizing orbital interactions are observed in acceptor[9].The strong intramolecular H-bonding explains the stability of the n-(3,4-diflurophenyl)-2,2-diphenylacetamide and increased the herbicidal activities of these compounds**.**

D. HOMO-LUMO ANALYSIS

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 0.33880 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[10]. The HOMO-LUMO energy separation can be used as a sign of kinetic stability.



HOMO **LUMO**

Fig 3. HOMO-LUMO Plots for N-(3,4-diflurophenyl)-2,2-diphenylacetamide

V. CONCLUSION

In the present work, complete vibrational analysis has been made for proper frequency contributions of n-(3,4-diflurophenyl)-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 red shifting 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-(3,4-diflurophenyl)-2,2-diphenylacetamide. 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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