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Quantum Chemical Computational Studies of Chlorophenylthiazolylnaphthylmethanone

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ABSTRACT

The compound's optimized geometry, bonding features, vibrational wave numbers, NBO analysis, and Mulliken population investigation on nuclear charges in the ground state were determined using Gaussian' 09 programme using the B3LYP technique with the 6-31G premise set. This work was completed with the aim of evaluating and planning quick, precise density functional theory (DFT) strategies for the compound. Particle computations have been improved, and they correlate with the trial values. The values of the electric dipole moment (μ) have been recorded using quantum mechanical ab initio and DFT estimation. However, the energy gap is a sign of polarizability, kinetic equilibrium, and chemical reactivity. The measured highest involved highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy gaps further support the existence of internal charge movement.

Keywords: optimized geometry, NBO analysis, Mulliken population, Gaussian's 09, DFT.

INTRODUCTION

Thiazoles and their analogues are used as starting materials for the production of molecules with biological activity[1]. They were said to have effects that were antibacterial[2-5], analgesic[6], anti-inflammatory[7], anticonvulsant[8], cardiotonic[9], anti-cancer[10-12], anti-tubercular[13], and anthelmintic[14]. Due to its natural occurrence in coal and petroleum products and emissions, its use as an intermediate in the production of plasticizers, resins, and insecticides, and its use in a variety of consumer products like moth repellants, naphthalene is frequently present in industrial and automotive emissions and effluents as well as in various media in the general environment[15]. Naphthalene is a smelly, poisonous substance with a variety of uses. Discover some of the most typical applications, risks, and safety precautions for naphthalene, which is even typically found under kitchen sinks[16].

Utilizing the 6-31G(d,p) basis sets, geometrical characteristics and vibrational frequencies of optimized compounds have been computed. Theoretically, other features like as Mulliken atomic charges, bond length, bond angle, HOMO, and LUMO were also discovered. Theoretical calculations were made to determine the electronic parameters FMO energy, softness, hardness, dipole moments, and electronegativity.

EXPERIMENTAL SECTION

Computational details

It has been established that quantum chemical computation is a vital tool for resolving intriguing chemical issues like to optimize the geometry, charge distribution, dipole moment, and localization of electrophilic and nucleophilic reactivity. Computational chemistry is a subfield of chemistry that uses computer simulation to address chemical issues. A career in computational chemistry necessitates patience, logical reasoning, and attention to detail in addition to an interest in statistical analysis techniques and computer modelling. In this sector, "people skills" are equally crucial. To set up the settings and parameters of their study, guarantee that the results are relevant, and ensure that the results are correctly understood, computational chemists must have a solid understanding of the fundamental concepts of a simulation, optimization, or other calculation[17].

Density Functional Theory

DFT is a computational quantum mechanical modelling technique which derives properties of the molecule primarily based on willpower of the electron density of the molecule, which is a physical function of all molecules. The electron density is a feature of three coordinates irrespective the electron number. Thus approximation, called local density approximation (LDA) is probably one of the most important concepts of DFT. The vibrational frequency and DFT (Density Functional Theory) calculation stage have been hired to use molecular geometry premiere structural and digital parameters to verify the shape as minima. To verify the shape as a minimum, molecular geometry optimized structural and electronic parameters have been employed on the vibrational frequency and DFT calculation degrees.

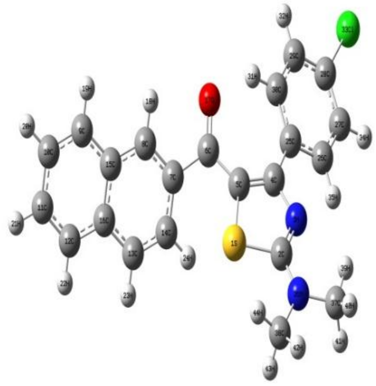
Gaussian 09

Gaussian 09 works from the fundamental legal guidelines of quantum mechanics. It predicts molecular structures, vibrational frequencies and numerous molecular properties of systems. All the theoretical calculations had been studied with Gaussian 09 program bundle and the calculated results had been visualized through Gauss View 5.0. The Becke-3Lee-Yang-Parr (B3LYP) degree DFT calculations were carried out the usage of the Gaussian 09 programme package deal with the common 6-31G basic set. In the programme for molecular visualisation, Gauss view 5.0.9, the vibrational frequency project and different parameters have been created. Every single calculation was executed in the gas phase segment the use of the optimized structures[18].

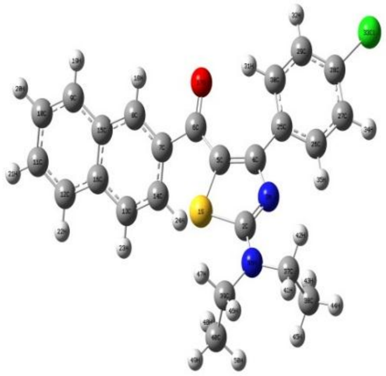
RESULTS AND DISCUSSION

Molecular geometry

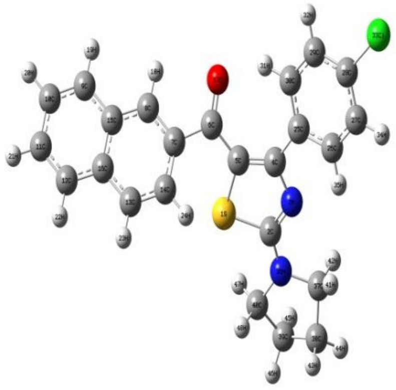
Molecular geometry through the numbering scheme of atoms is acquired from Gaussian 09 package. Minimum energy obtained by DFT structure optimization using 6-31G (d,p) basis set. The structural parameters like bond length, bond angle and dihedral angle were calculated and shown in **table 2 and figure 1.** The C-S bond length is greater than C-C, C-N, C-O and C-H bonds because the size of the atoms increases bond length also increases. In order to bond length is C-S > C-C > C-N > C-O > C-H. The Self-Consistent Field (SCF) energy of target compounds at a B3LYP level within the basis set 3-21G is found to be -1881.8 a.u, -1960.0 a.u, 1958.8 a.u, 1997.9 a.u and 2043.9 a.u with dipole moment 8.006, 8.029, 8.685, 8.292 and 6.485 Debye. From these evidences, the compound was formulated as chlorophenylthiazolylnaphthylmethanone in **(Table: 1)**. The optimized figure is given below **(Figure: 1)**,



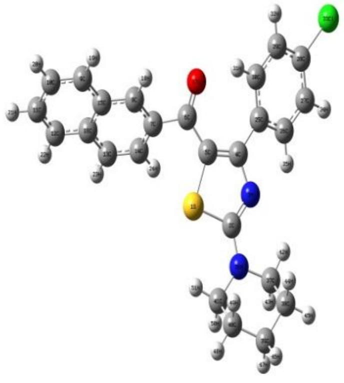
2a



2b



2c



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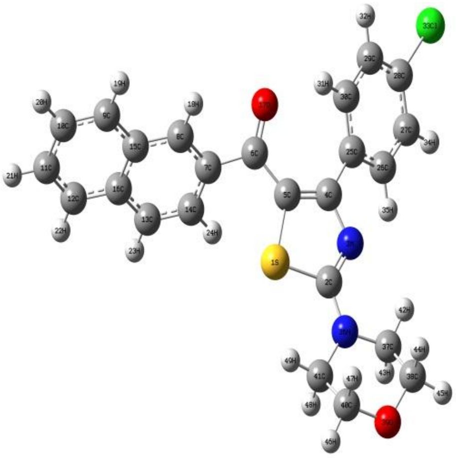


2e

Figure 1: Optimized structure of chlorophenylthiazolylnaphthylmethanone

Data of chlorophenylthiazolylnaphthylmethanone Abbreviations:

2a – (4-chlorophenyl-2-dimethylaminothiazol-5-yl-2-naphthyl)methanone

2b – (4-chlorophenyl-2-diethylaminothiazol-5-yl-2-naphthyl)methanone

2c – (4-chlorophenyl-2-pyrrolidin-1-ylthiazol-5-yl-2-naphthyl)methanone

2d – (4-chlorophenyl-2-piperidin-1-ylthiazol-5-yl-2-naphthyl)methanone

2e – (4-chlorophenyl-2-morpholin-1-ylthiazol-5-yl-2-naphthyl)methanone

Table: 1 Calculated electronic parameters

Parameters (a.u)	**2a**	**2b**	**2c**	**2d**	**2e**
Total Energy (a.u)	-1881.85	-1960.06	-1958.86	-1997.96	-2043.96
Dipole Moment (Debye)	8.0066	8.0293	8.6854	8.2922	6.4855
HOMO	-0.2418	-0.2417	-0.2405	-0.2408	-0.2397
LUMO	-0.0353	-0.0346	-0.0318	-0.0338	-0.0371
HOMO-LUMO (ΔE)	0.2065	0.2071	0.2087	0.2070	0.2026
Ionisation potential (I)	0.2418	0.2417	0.2405	0.2408	0.2397
Electron affinity (A)	0.0353	0.0346	0.0318	0.0338	0.0371
Electronegativity (χ)	0.1385	0.1381	0.1361	0.1373	0.1384
Hardness (η)	0.1032	0.1035	0.1043	0.1035	0.1013
Softness (S)	4.8449	4.8309	4.7938	4.8309	4.9358

Data of chlorophenylthiazolylnaphthylmethanone

Table 2: Bond length data

Position	Parameter	2a	2b	2c	2d	2e
Thiazole	C-S	1.835	1.837	1.832	1.838	1.828
Thiazole	C=N	1.389	1.390	1.389	1.388	1.392
Naphthalene	C-C	1.421	1.376	1.376	1.376	1.380
Naphthalene	C-H	1.084	1.083	1.083	1.083	1.085
Phenyl	C-C	1.395	1.395	1.395	1.395	1.399
Phenyl	C-H	1.081	1.081	1.081	1.081	1.083
Phenyl	C-Cl	1.834	1.834	1.834	1.834	1.828
Chain	C=O	1.083	1.254	1.254	1.254	1.261
Chain	N-C	1.347	1.345	1.336	1.345	1.355
Chain	C-H	1.093	1.095	1.092	1.096	1.099
Chain	C-O	-	-	-	-	1.461

Bond angle data

Position	Parameter	2a	2b	2c	2d	2e
Thiazole	S-C-N	113.8	113.7	114.3	114.4	114.4
Thiazole	N-C-C	115.7	115.5	115.8	115.4	115.7
Naphthalene	C-C-C	122.4	122.4	122.4	122.4	122.4
Naphthalene	H-C-C	119.4	119.4	119.4	119.4	119.4
Phenyl	C-C-C	118.5	118.5	118.5	118.5	118.5
Phenyl	H-C-C	120.5	120.5	120.5	120.5	120.5
Phenyl	Cl-C-C	119.0	119.0	119.0	119.0	119.2
Chain	O-C-C	117.8	117.8	117.7	117.8	117.8
Chain	C-N-C	119.3	118.0	121.7	120.1	122.1
Chain	H-C-H	108.9	-	109.7	-	-
Chain	C-C-O	-	-	-	-	110.5

Dihedral angle data

Position	Parameter	2a	2b	2c	2d	2e
Thiazole	S-C-N-C	176.9	177.5	-177.3	177.3	176.0
Thiazole	N-C-C-C	-160	115.5	115.8	115.4	115.7
Naphthalene	C-C-C-C	-179.2	-179.3	179.6	-179.3	-179.7
Naphthalene	H-C-C-C	-178.4	-179.5	178.5	-178.5	-178.7
Phenyl	H-C-C-C	-179.6	-179.5	179.5	-179.6	-179.8
Phenyl	Cl-C-C-C	179.7	179.7	-179.7	179.7	179.7
Chain	S-C-C-O	147.6	147.9	-148.9	147.4	145.9
Chain	C-N-C-C	-	-81.4	168.0	118.1	135.4
Chain	H-C-C-O	-	-	-	-	173.7

Frontier molecular orbital studies

The electronic properties of isolated molecules are associated to its geometry. It is also gives knowledge about macroscopic characteristics of a molecular system in condensed phase. The frontier molecular orbitals allow identifying the most important interaction sites susceptible to electrophilic and nucleophilic attacks of a molecule pharmacological interest[19]. The difference between HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) is called Energy gap (ΔE) **(Table: 1)**. HOMO & LUMO of chlorophenylthiazolylnaphthylmethanone in **(Figure: 2)**,

Koopmans' equation

The orbital frontier molecular orbital energies are listed below with I = ionisation potential

$-\varepsilon HOMO = I$ and

$-\varepsilon LUMO = A$, respectively. 1

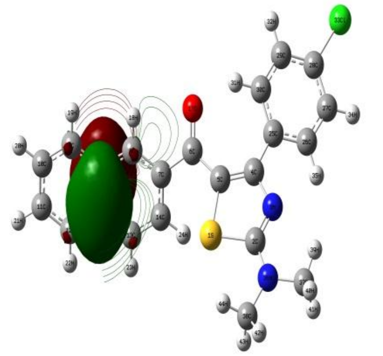
The electron affinity is A.

The HOMO energy and LUMO energy of the electronic parameters shown in **Table -1** can be used to compute the absolute electro negativity (χ), total hardness (H), and softness (S).

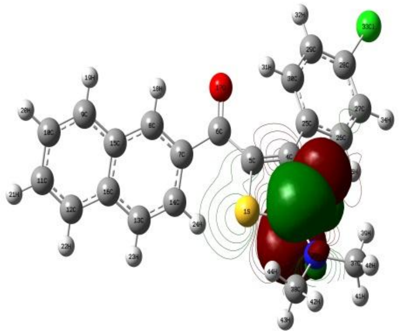
$(\chi) = (I+A) / 2$; $\eta = (I-A) / 2$ and

$S = 1 / (2\times\eta)$ 2

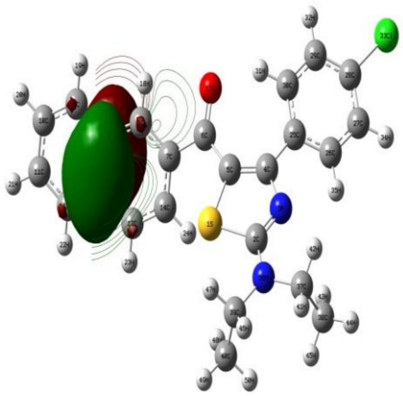
The electro negativity (χ), hardness (H), and softness (S) are calculated using the eqn 2, which is presented in **Table -1**.



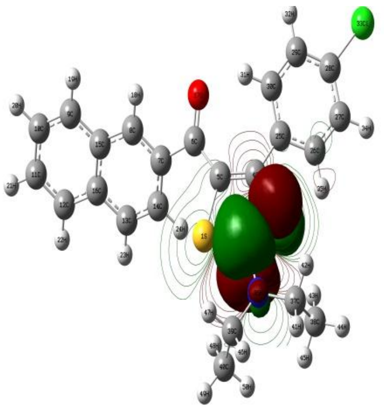
2a (HOMO)



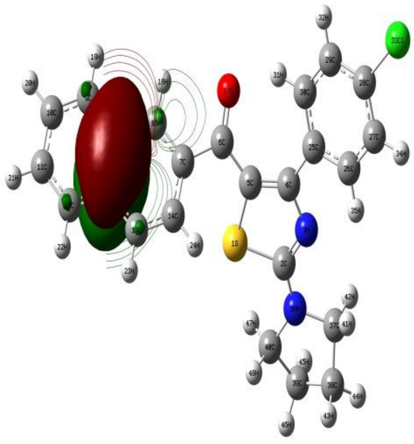
2a (LUMO)



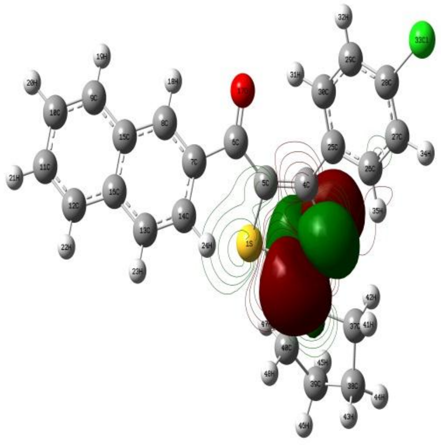
2b (HOMO)



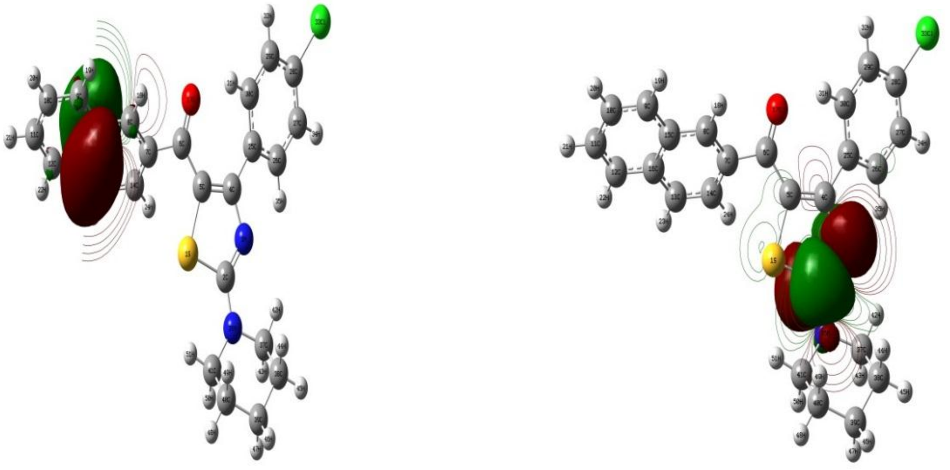
2b (LUMO)



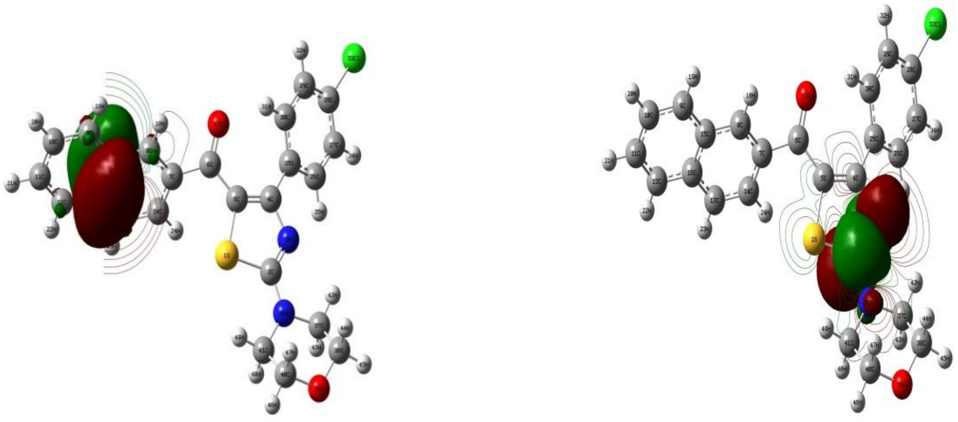
2c (HOMO)



2c (LUMO)



2d (HOMO) **2d (LUMO)**

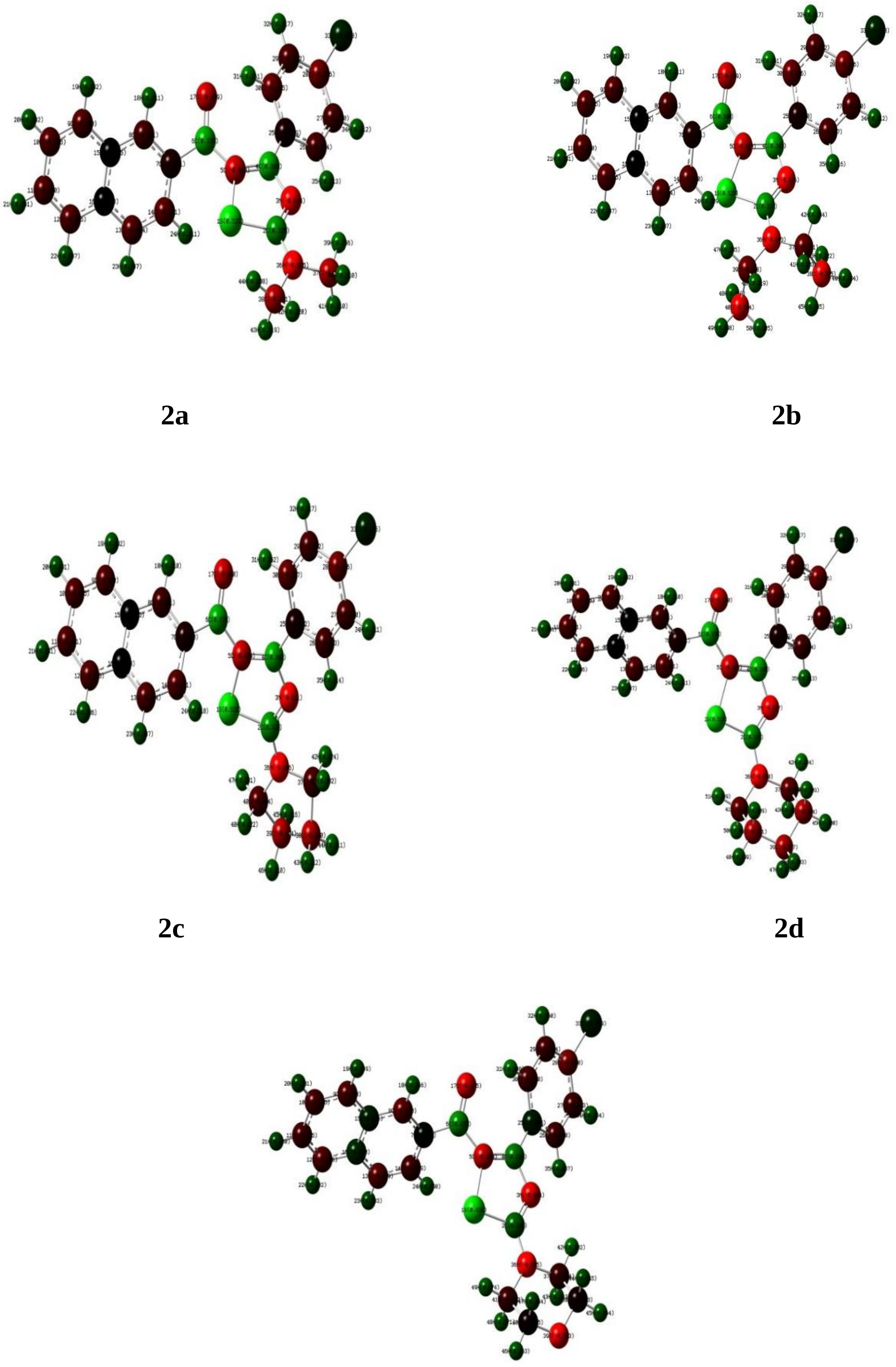


2e (HOMO) **2e (LUMO)**

Figure: 2 HOMO & LUMO of chlorophenylthiazolylnaphthylmethanone

Mulliken charge distribution

Mulliken population analysis is a quantum chemical calculation that determines atoms' charge distribution using computational chemistry techniques[20]. The linear combination of atomic orbitals molecular orbital (LCAO) approach is specifically used to calculate Mulliken charges. Based on the B3LYP/6-31G (d,p) model, the solvent effect for the atomic charge distributions of generated compounds. All nitrogen and oxygen carry negative charges, while hydrogen, sulphur, and chlorine carry positive charges, and carbon can carry either a positive or negative charge depending on the atoms nearby **(Fig. 3)** and **(Table: 3**). Positively charged atoms are an electron-donating group, whereas negatively charged species are electron acceptors.



2a **2b**

2c **2d**

2e

Figure: 3 Mulliken atomic charge of chlorophenylthiazolylnaphthylmethanone

Table: 3 Mulliken charges of chlorophenylthiazolylnaphthylmethanone

Atom	**Mulliken Charges 2a**	**Mulliken Charges 2b**	**Mulliken Charges 2c**	**Mulliken Charges 2d**	**Mulliken Charges 2e**
S_1	0.523	0.523	0.522	0.516	0.438
C_2	0.325	0.327	0.323	0.327	0.183
N_3	-0.614	-0.616	-0.611	-0.617	-0.464
C_4	0.385	0.382	0.382	0.385	0.226
C_5	-0.463	-0.463	-0.459	-0.463	-0.389
C_6	0.379	0.380	0.378	0.378	0.257
C_7	-0.071	-0.071	-0.070	-0.071	0.013
C_8	-0.151	-0.151	-0.151	-0.151	-0.170
C_9	-0.180	-0.180	-0.180	-0.180	-0.143
C_{10}	-0.185	-0.185	-0.185	-0.185	-0.135
C_{11}	-0.180	-0.180	-0.181	-0.181	-0.125
C_{12}	-0.185	-0.185	-0.185	-0.185	-0.156
C_{13}	-0.184	-0.184	-0.184	-0.184	-0.169
C_{14}	-0.191	-0.190	-0.191	-0.191	-0.119
C_{15}	-0.005	-0.005	-0.005	-0.005	0.056
C_{16}	0.003	0.003	-0.003	0.003	0.080
O_{17}	-0.459	-0.459	-0.460	-0.460	-0.435
H_{18}	0.211	0.211	0.210	0.210	0.166
H_{19}	0.192	0.192	0.192	0.192	0.139
H_{20}	0.192	0.192	0.191	0.191	0.131
H_{21}	0.191	0.191	0.191	0.191	0.130
H_{22}	0.187	0.187	0.186	0.186	0.132
H_{23}	0.187	0.187	0.187	0.187	0.133
H_{24}	0.211	0.209	0.210	0.211	0.150
C_{25}	-0.059	-0.060	-0.062	-0.059	0.055
C_{26}	-0.154	-0.157	-0.153	-0.154	-0.120
C_{27}	-0.160	-0.160	-0.160	-0.160	-0.113

C_{28}	-0.256	-0.256	-0.256	-0.256	-0.220
C_{29}	-0.162	-0.162	-0.162	-0.162	-0.124
C_{30}	-0.225	-0.226	-0.227	-0.226	-0.130
H_{31}	0.261	0.261	0.262	0.261	0.208
H_{32}	0.217	0.217	0.217	0.217	0.160
Cl_{33}	0.078	0.078	0.076	0.077	0.059
H_{34}	0.212	0.212	0.211	0.211	0.154
H_{35}	0.213	0.216	0.214	0.213	0.157
N_{36}	-0.655	-0.643	-0.666	-0.650	-0.565
C_{37}	-0.391	-0.211	-0.166	-0.210	-0.104
C_{38}	-0.391	-0.565	-0.410	-0.374	-0.033
H_{39}	0.256	-	-	-	-
C_{39}	-	-0.228	-0.404	-0.377	-
O_{39}	-	-	-	-	-0.503
C_{40}	0.210	-0.564	-0.184	-0.371	-0.025
H_{41}	0.210	0.203	0.232	-	-
C_{41}	-	-	-	-0.212	-0.113
H_{42}	0.220	0.244	0.224	0.254	0.202
H_{43}	0.219	0.222	0.212	0.207	0.163
H_{44}	0.238	0.194	0.211	0.209	0.145
H_{45}	-	0.195	0.216	0.200	0.164
H_{46}	-	0.219	0.210	0.203	0.163
H_{47}	-	0.235	0.231	0.188	0.144
H_{48}	-	0.218	0.222	0.199	0.171
H_{49}	-	0.198	-	0.209	0.174
H_{50}	-	0.205	-	0.216	-
H_{51}	-	-	-	0.239	-

CONCLUSION

In conclusion, we have developed a workable method and appropriate conditions for reactions to yield derivatives of chlorophenylthiazolylnaphthylmethanone. DFT/B3LYP techniques were used to optimize the geometry of the derivatives of chlorophenylthiazolylnaphthylmethanone utilising 6-31G (d,p) basis sets. The optimized geometry of the molecules, molecular structural parameters and electronic characteristics has been calculated using ab initio and DFT methods. The greatest and shortest bond distances are S_1-C_2 and C_{26}-H_{35}, respectively. Therefore, the longest S_1-C_2 distance reveals the single bond character in its purest form. The intramolecular charge transfer via the conjugated system was explained by HOMO-LUMO investigations. Frontier molecular orbitals, which ensure charge transmission within the molecule, include the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). The molecules are more bioactive because the HOMO-LUMO energy gap is less. N_{36} has a higher negative Mulliken atomic charge, while S_1 has a higher positive charge.

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DECLARATION OF COMPETING INTERESTS

All authors declare no competing interest regarding the publication of this article.

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