



Synthesis, Spectral and DFT Analysis of Novel Trifluoromethoxy based Oxadiazole

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KEYWORDS

1,3,4-oxadiazole,
Spectral study,
HOMO-LUMO,
vibrational analysis
and NLO property.

ABSTRACT:

In this study, we began by 5-bromo-2-(trifluoromethoxy)benzoic acid and successfully synthesized a novel compound, namely 2-(5-bromo-2-(trifluoromethoxy)phenyl)-5-(furan-2-yl)-1,3,4-oxadiazole. The structural characterization of the newly synthesized derivatives was confirmed using a combination of analytical techniques, proton nuclear magnetic resonance (¹H NMR), carbon-13 nuclear magnetic resonance (¹³C NMR), and infrared (IR) spectroscopy. Furthermore, the theoretical computation of 2-(5-bromo-2-(trifluoromethoxy)phenyl)-5-(furan-2-yl)-1,3,4-oxadiazole was conducted using Density Functional Theory (DFT) with the Becke, three-parameter, Lee-Yang-Parr (B3LYP) dicey functional and the 6-311+G(d,p) basis set. Analysis was done on the computed values of geometric structural parameters, polarizability along with hyperpolarizability, nucleus-independent chemical shifts, NMR spectra, highest occupied as well as lowest unoccupied molecular orbitals, and Fourier transform infrared spectral data.

1. Introduction

Its commonly recognized in the literature that chemicals containing N, O, as well as sulfur are mostly utilized in medicine to treat bacterial and fungal infections, as well as gastric ulcers, cancer, and other conditions. Higher effectiveness against a variety of ailments is the outcome of the organic moiety's nitrogen atom [1]. Heterocyclic compounds with five members exhibit a variety of biological functions. Wide-ranging properties like antibacterial [2], antimalarial [3], anti-inflammatory [4], antifungal [5], as well as anticonvulsant [6] are also exhibited by 2,5-Disubstituted 1,3,4-oxadiazoles. A increasing amount of articles and patents attest to the significant pharmaceutical and material interest in substituted 1,3,4-oxadiazoles. Such as, 2-amino-1,3,4-oxadiazoles have antimitotic action along with relax muscles [6]. Dyes of 5-aryl-2-hydroxymethyl-1,3,4-oxadiazole contains analgesic, non-inflammatory, anticonvulsive, diuretic, as well as antiemetic effects [7]. Liquid crystals and photosensitizers are two material uses of 1,3,4-oxadiazole derivatives [8]. Common synthesis methods for oxadiazoles [9] include diacylhydrazine cyclization. The cyclization process is influenced by a number of reaction circumstances. Heat as well as dehydrated reagents such as thionyl chloride,

phosphorous oxychloride [10], phosphorous pentoxide [11], triphenylphosphine [12], Lawesson's reagent [13], and triflic anhydride are commonly used to facilitate the reaction. Additional synthesis methods include the base-catalyzed cyclization reaction of trichloroacetic acid hydrazones and the reaction between carboxylic hydrazides and ketenylidene triphenyl phosphorane.

2. Experimental

All of the chemicals (reagents as well as solvents) were bought from overseas businesses (Sigma/Aldrich and Hi-Media). TLC was used to identify, purify, and scale the produced chemicals for yield. The Shimadzu 8201PC equipment, which operates on 4000-400 cm⁻¹, was used to record the ultraviolet spectra (KBr). The Agilent V NMRS-400 instrument was used to record the proton and co NMR spectra with CDCl₃. The chemical shifts are reported in parts per million.

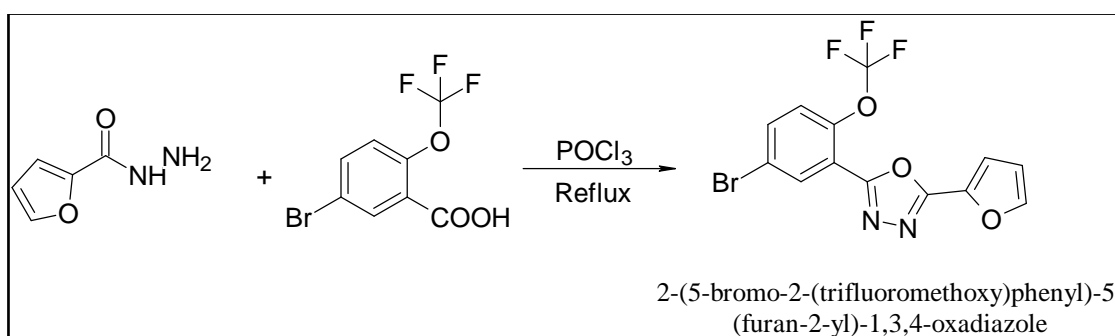
2.1. Synthesis of 2-(5-bromo-2-(2-trifluoromethoxy)phenyl)-5-aryl-1,3,4-oxadiazole 3(a-g):

After dissolving 1 mmol of furan-2-carbazide in 5 mL of phosphorous oxychloride, 1 mmol of 5-bromo-2-(2-trifluoromethoxy)benzoic acid was added to a round-bottom flask [14]. This mixture had minor reflux.



Following the reaction conclusion, the fluid was allowed to cool to room temperature before being poured over crushed ice. A solid mass was separated after the content were normalized with a 20% NaHCO₃ solution. This were made into 2-(5-bromo-2-(2-trifluoromethoxy)phenyl)-5-aryl-1,3,4-oxadiazole by

filtering, washing, and recrystallizing it with ethanol which melts on 125-126°C (**Scheme-1**). The alternative aromatic acids were preferred as a widely initiating matter for the synthesis of 1,3,4-oxadiazoles derivatives carrying the formation of corresponding esters as well as hydrazides.



Scheme-1. Synthesis scheme for 2-(5-bromo-2-(trifluoromethoxy)phenyl)-5-(furan-2-yl)-1,3,4-oxadiazole

2.2. Computational details

The Gaussian 09 program package was used to do the quantum chemistry calculations of BDMB at the DFT/B3LYP/6-311G (d, p) level of theory [15]. At the DFT level, the initial geometry produced by geometrical parameters was reduced in the potential energy surface without any constraints. All stationary sites were classified as minima using the vibrational wavenumber calculations using the optimized minimum structure specifications. We calculated harmonic vibrational wavenumbers and the corresponding Raman depolarization ratios as well as FT-IR sensitivities. Using the VEDA-4 program, the vibrational modes were allocated according to the potential energy distribution. The Raint program was used to convert the Raman activities into relative Raman intensities [16].

3. Results & Discussion

3.1. Optimized parameters

Table 1 displays the optimum parameters that were calculated. 2-(5-bromo-2-(trifluoromethoxy)phenyl)-5-(furan-2-yl)-1,3,4-oxadiazole's optimal molecular structure is displayed in **Figure 1**. Two C-O-C bonds, two N=C bonds, one C-Br bond, three C-F bonds, six C-H bonds, and four C-C bonds are present in the molecule under investigation. Furan, oxadiazole, and one bromo ring make up the chemical being studied. The phenyl ring's C-C bond lengths range from 1.386 to 1.4098 Å.

Because of the electron withdrawing groups in ortho position, the bond between C14-C15 and C14-C16 is longer, measuring 1.2757 and 1.2747 Å. The compound's calculated C=N bonds in this study are approximately 1.30 Å, while its XRD values fall between 1.2751 and 1.2741 Å. In the oxadiazole circle, the ideal bond between C and O distance ranges from 1.3747 to 1.3782 Å, and it is comparable to the value of 103.84 Å reported in the literature. The total length of the N5-N4 bond is 1.4522 Å, which is more than the figure of 1.4221 Å reported in the literature. The molecule has a twist when matching the phenyl ring versus the trifluoromethyl oxadiazole group, which results from the dihedral angle of 121.0279 Å.

Table-1: Bond parameters of 2-(5-bromo-2-(trifluoromethoxy)phenyl)-5-(furan-2-yl)-1,3,4-oxadiazole

Bond	Bond length	Bond	Bond angle	Bond	Dihedral angle
C1-O2	1.3782	O2-C1-N4	112.0646	N4-C1-O2-C3	-0.157
C1-N4	1.2757	O2-C1-C6	115.7523	C6-C1-O2-C3	179.77



C1-C6	1.425 5	N4-C1-C6	132.183	O2-C1-N4-N5	0.0544
O2-C3	1.374 4	C1-O2-C3	103.832 9	C6-C1-N4-N5	- 179.843
C3-N5	1.274 1	O2-C3-N5	111.560 7	O2-C1-C6-O7	- 179.963
C3-C11	1.453 2	O2-C3-C11	120.875 6	O2-C1-C6-C8	0.018
N4-N5	1.452 2	N5-C3-C11	127.540 7	N4-C1-C6-O7	-0.069
C6-O7	1.37	C1-N4-N5	105.746	N4-C1-C6-C8	179.912
C6-C8	1.343 9	C3-N5-N4	106.795 4	C1-O2-C3-N5	0.209
O7-C9	1.376 2	C1-C6-O7	119.904 8	C1-O2-C3-C11	178.591
C8-C10	1.440 6	C1-C6-C8	129.648 8	O2-C3-N5-N4	-0.182
C8-H28	1.063 7	O7-C6-C8	110.446 4	C11-C3-N5-N4	- 178.429
C9-C10	1.344 1	C6-O7-C9	106.706 7	O2-C3-C11-C12	10.196
C9-H26	1.061 5	C6-C8-C10	106.207 7	O2-C3-C11-C13	- 169.781
C10-H27	1.063 9	C6-C8-H28	125.687 7	N5-C3-C11-C12	- 171.703

C11-C12	1.381 5	C10-C8-H28	128.104 6	N5-C3-C11-C13	8.321
C11-C13	1.389 2	O7-C9-C10	109.877	C1-N4-N5-C3	0.079
C12-C14	1.375 6	O7-C9-H26	116.147 7	C1-C6-O7-C9	179.976
C12-O21	1.401 7	C10-C9-H26	133.975 3	C8-C6-C7-C9	-0.008
C13-C15	1.371 8	C8-C10-C9	106.762 2	C1-C6-C8-C10	- 179.978
C13-H16	1.068 7	C8-C10-H27	126.520 2	C1-C6-C8-H28	0.045
C14-C17	1.379 7	C9-C10-H27	126.717 6	O7-C6-C8-C10	0.005
C14-H18	1.069 1	C3-C11-C12	123.358 1	O7-C6-C8-H28	- 179.973
C15-C17	1.378 5	C3-C11-C13	117.988 5	C6-O7-C9-C10	0.009
C15-Br20	1.918 5	C12-C11-C13	118.653 5	C6-O7-C9-H26	- 179.981
C17-H19	1.068 9	C11-C12-C14	121.027 9	C6-C8-C10-C9	0.001
O21-C22	1.351	C11-C12-O21	120.357 5	C6-C8-C10-H27	179.983
C22-F23	1.333 1	C14-C12-O21	118.546 5	H28-C8-C10-C9	179.978



C22-F24	1.343 4	C11-C13-C15	120.429 5	H28-C8-C10-H27	-0.041
C22-F25	1.337 6	C11-C13-H16	118.767 8	O7-C9-C10-C8	-0.006
		C15-C13-H16	120.802 2	O7-C9-C10-H27	-179.988
		C12-C14-C17	119.748 1	H26-C9-C10-H27	179.981
		C12-C14-H18	119.036 9	H26-C9-C10-H27	-0.00
		C17-C14-H18	121.213 2	C3-C11-C12-C14	-179.058 2
		C13-C15-C17	120.366 2	C3-C11-C12-O21	3.987
		C13-C15-Br20	119.825 4	C13-C11-C12-C14	0.9181
		C17-C15-Br20	119.808 3	C13-C11-C12-O21	-176.036 7
		C14-C17-C15	119.768 4	C3-C11-C13-C15	179.251 5
		C14-C17-H19	120.265 1	C3-C11-C13-H16	-0.4904
		C15-C17-H1	119.965 9	C12-C11-C13-C15	-0.726
		C12-O21-C22	122.044 1	C12-C11-C13-H16	179.532

		O21-C22-F23	108.950 7	C11-C12-C14-C17	-0.4358
		O21-C22-F24	111.029 2	C11-C12-C14-H18	-179.944 7
		O21-C22-F25	112.390 5	O21-C12-C14-C17	176.572 9
		F23-C22-F24	108.114 3	O21-C12-C14-H18	-2.936
		F23-C22-F25	109.007 8	C11-C12-O21-C22	-99.5224
		F24-C22-F25	107.238	C14-C12-O21-C22	83.4481
				C11-C13-C15-C17	0.0562
				C11-C13-C15-Br20	-179.846 9
				H16-C13-C15-C17	179.792 8
				H16-C13-C15-Br20	-0.1103
				C12-C14-C17-C15	-0.2517
				C12-C14-C17-H19	-179.975 4
				H18-C14-C17-C15	179.246 3
				H18-C14-	-0.4774



				C17-H19	
				C13-C15-C17-C14	0.4393
				C13-C15-C17-H19	-179.8362
				Br20-C15-C17-C14	-179.6576
				Br20-C15-C17-H19	0.0669
				C12-O21-C22-F23	160.1849
				C12-O21-C22-F24	-80.8554
				C12-O21-C22-F25	39.2611

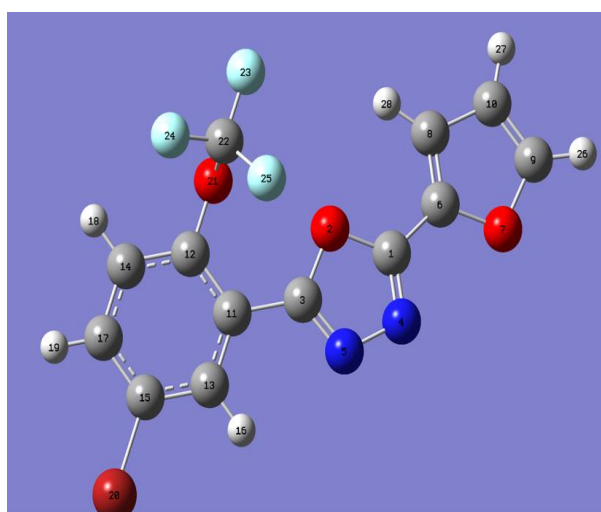


Figure 1: 2-(5-bromo-2-(trifluoromethoxy)phenyl)-5-(furan-2-yl)-1,3,4-oxadiazole's optimized molecular structure.

3.2. NLO Properties

The importance of nonlinear optical related studies in giving the essential functionality of optical tranfering, optical modulation, optical scenario, as well as optical storage for the new methods in fields like signal authenticating, telecommunications, as well as optical inbetween connections has put them at the forefront of research these days [17, 18]. It was determined (**Table-2**) that the molecule polarizability was -131.789 esu, while the hyperpolarizability was 9.1×10^{-31} esu. The reference urea and the title molecule have nearly identical β_0 values. One with good non-linear optical properties is urea, which is employed as a crucial parameter for comparison research ($\beta = 3.7289 \times 10^{-31} \text{ am}^5/\text{e.s.u.}$ and $\mu = 1.3732$ Debye) [19].

Table 2: Non-linear optical characteristics of 5-(furan-2-yl)-5-(5-bromo-2-(trifluoromethoxy)phenyl) 1,3,4-oxadiazole

Parameters	DFT	Hyperpolarizability	
Dipole moment		β_{xxx}	69.0393
μ_x	0.1354	β_{yyy}	73.1287
μ_y	4.0071	β_{zzz}	16.7337
μ_z	-0.1391	β_{xyy}	-72.466
μ	4.0118	β_{xxy}	12.3686
Polarizability		β_{xxz}	9.0326
α_{xx}	-106.46	β_{xzz}	-42.833
α_{yy}	-148.00	β_{yzz}	5.2606
α_{zz}	-140.92	β_{yyz}	2.0672
α_{xy}	-2.01	β_{xyz}	5.695
α_{yz}	1.57	β_{tot}	105.602
α_{yz}	-1.54	β_0	9.1×10^{-31}
α_0	-1.95E-23		
α	-131.7896667		



3.3. Molecular electrostatic potential (MEP)

Since the positively charged regions act as nucleophilic sites, while the negatively charged regions are more prone to function as electrophilic sites, the Molecular Electrostatic Potential (MEP) surface provides valuable insights into a molecule's reactivity. **Figure 2** illustrates that the nucleophilic center appears as the positive (blue) region on the MEP surface, whereas the electrophilic region corresponds to the negative (red) region. Additionally, same as colour transitions following red to orange, after that to yellow, green, and finally blue, the electrostatic capacity increases. The Furan carbon, oxadiazole nitrogen, and bromine atoms are all subject to the compound's negative potential, which begins at -7.570×10^{-2} . It is vulnerable to electrophilic assault and could be caused by the delocalization of π -electrons. The blue-colored areas close to sulfur are not ideal for electrophilic assault. [20,21].

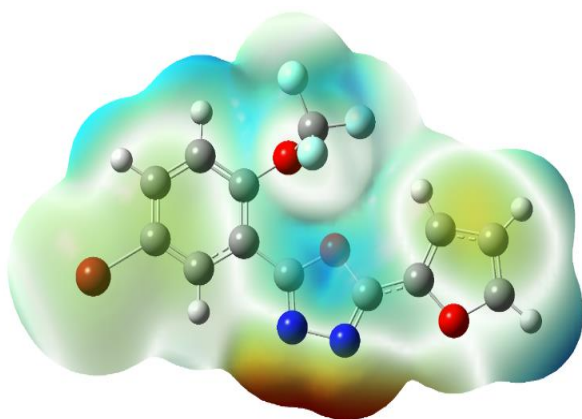


Figure 2: MEP diagram of 5-(furan-2-yl)-5-(5-bromo-2-(trifluoromethoxy)phenyl) 1,3,4-oxadiazole

3.4. FMO Analysis

Both the "highest molecular orbital (HOMO)" and the "lowest unoccupied molecular orbital (LUMO)" are included. The DFT/B3LYP/6-311(d,p) level was used to compute the FMO energies of the molecule being studied. The values are provided by **Table 2**. The HOMO lobes are partially oriented on the imidazole and furan rings, and partially on the phenyl moiety which are shown in **Figure 3**. On the other hand, LUMO concentrates on the phenyl ring and imidazole molecule. The HOMO and LUMO energy gaps were found to be 3.2911 eV. The value is so small even though the molecule should have more transitions [22-24]. A molecule's equilibrium,

toughness, suppleness, and responsiveness are frequently described by its energy gap. A high energy gap indicates greater hardness, non-reactivity, and large stability of the compounds being studied. The energy capacity of FMOs are used to calculate the global reactivity areas (GRPs).

The molecule exhibited a significant electron affinity of -5.017 eV and a calculated ionization potential of -8.307 eV. Additionally, it demonstrated a higher global hardness value, indicating its resistance to deformation by external influences. The electronegativity amplitude was determined to be -6.662 eV. To assess the stability and reactivity of the compound, chemical potential amplitudes were analyzed. Generally, compounds with lower chemical potential values are considered less reactive and more stable, whereas those with higher chemical potential values exhibit greater reactivity. The molecule under investigation had a global electrophilicity (ω) value of 13.489 eV and a chemical potential (μ) of -4.0763 eV. The findings clearly indicate that the computed electron affinity was significantly lower than the observed ionization potential values [25, 26]. This strong discrepancy provides substantial evidence supporting the electron-giving capability of the studied compounds.

Table 3: Electronic descriptors calculated by B3LYP/6-31G (d, p) method

Parameters	Energy (Ev)
E_{HOMO}	-8.307
E_{LUMO}	-5.017
ΔE	3.291
Electronegativity (χ)	-6.662
Hardness(η)	1.645
Electrophilicity index(ω)	13.489
Softness(s)	225.006
Dipole moment (μ)	4.0118

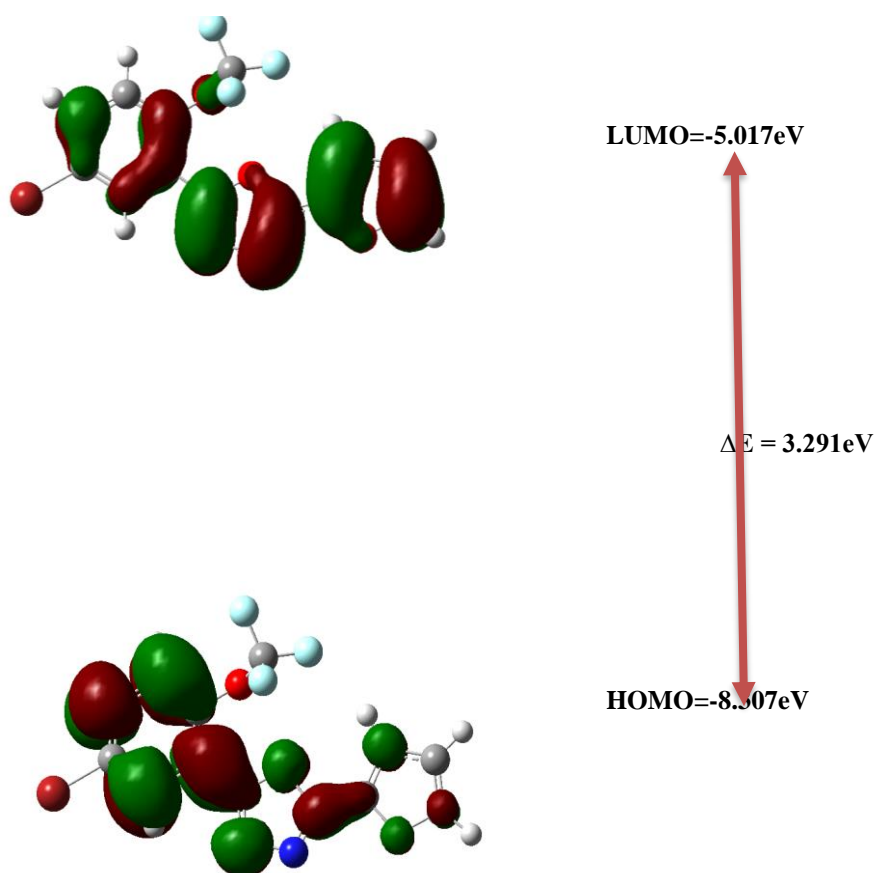


Figure 3 : HOMO and LUMO diagram of 5-(furan-2-yl)-5-(5-bromo-2-(trifluoromethoxy)phenyl) 1,3,4-oxadiazole

These researches depicted that all entitled compounds were chemically tough along with best kinetic stability as well as electron-donating ability.

3.5. Vibrational analysis:

This 28-atom compound, 2-(5-bromo-2-(trifluoromethoxy)phenyl)-5-(furan-2-yl)-1,3,4-oxadiazole, has symmetry in the C₁ point group. The nonlinear molecule's fundamental modes of vibration are (3N-6), where N is the total quantity of atoms in the molecule. As a result, there are 78 fundamental modes of vibration in the title molecule. These modes of vibration are predicted theoretically and empirically, and the values are shown in **Table 4**. **Figure 4** display the title molecule's theoretical and empirical spectra, respectively. Because of the anharmonic character of vibrations and the unexpected distribution of electrons in the bonds, the examined wavenumbers are marginally larger than the

experimental values. The wavenumber was scaled by a scaling factor of 1.002.

3.5.1 Furan ring vibration:

Three C-C expanding vibrations, 3 C-H expanding vibrations, and two C-O stretching vibrations make up the furan. It is anticipated that C=C stretching vibrations would occur between 1600 and 1490 cm⁻¹, whereas C-H vibrations will occur between 1449 and 1398 cm⁻¹ [14]. In this instance, the O-C vibration was detected at 7444 cm⁻¹, and the C=C vibration was detected in the range 1637-1478 cm⁻¹, which is similar to the experimental range 1153-1142 cm⁻¹. Because of how the electrons are distributed in these bonds, the vibrational frequencies show a tiny drop and increase, indicating a weakening of the connection. The experimental values of 3084 and 2947 cm⁻¹, respectively, are consistent with the C-H stretching modes of vibration,



which were detected at 3543 and 3267. S8-C11-C9 Both in-plane and out-of-plane C-O bending vibrations are detected in the 863 and 662 cm⁻¹ regions, respectively.

Pyrazole ring is attached with the oxadiazole functional group, in which there is two C-O stretching vibration is present, the C-O extending vibrations [14]

were observed in the area of 1378-1093 cm⁻¹ in the studied compound which closer to the experimental range of 1449-1341 cm⁻¹. This observed result is though well agreed with the expected values, there are slight deviations which account for the variation in the conjugational pattern in the molecule.

Table 4: Vibrational Assignment of 2-(5-bromo-2-(trifluoromethoxy)phenyl)-5-(furan-2-yl)-1,3,4-oxadiazole

Mode no.	Unscaled wave number	Scaled wave number	FT-IR	PED _≥ (100%)
1	3507	3653.13		□□C8-H28+□□C9-H26+□□C10-H27 (81)
2	3491	3636.46		□□C8-H28+□□C9-H26+□□C10-H27 (79)
3	3463	3607.29		□□C8-H28+□□C9-H26+□□C10-H27 (79)
4	3417	3559.38		□□C13-H16+□□C14-H18+□□C17-H19 (83)
5	3415	3557.29		□□C13-H16+□□C14-H18+□□C17-H19 (40)
6	3402	3543.75	3084.51	□□C13-H16+□□C14-H18+□□C17-H19 (48)
7	1841	1917.71	1907.71	□□N4-C1+□□N5-C3 (18)
8	1841	1917.71		□□C8-C6+□□C10-C9+□□C11-C12 (16)
9	1787	1861.46		□□C12-C14+□□C13-C15+□□C15-C17+ □ C17-C14 (30)
10	1726	1797.92		□□C12-C14+□□C13-C15+□□C15-C17+ □ C17-C14 (16)
11	1706	1777.08	1753.76	□□N4-C1+□□N5-C3 (19)
12	1658	1727.08		□ H16-C13-C15+□ H18-C14-C17+□ H19-C17-C15 (44)
13	1607	1673.96		□□C8-C6+□□C10-C9+□□C11-C12 (25)
14	1607	1673.96	1637.54	□□C8-C6+□□C10-C9+□□C11-C12 (31)
15	1561	1626.04	1599.31	□ C11-C12-C14+□ C12-C14-C17+□ C13-C15-C17+□ C15-C17-C14 (17)
16	1539	1603.13	1582.83	□ H27-C10-C8+□ H28-C8-C10 (20)
17	1489	1551.04	1524.65	□□F23-C22+□□F24-C22+□□F25-C22 (44)
18	1472	1533.33		□ H16-C13-C15+□ H18-C14-C17+□ H19-C17-C15 (31)
19	1432	1491.67	1494.36	□□F23-C22+□□F24-C22+□□F25-C22 (30)
20	1420	1479.17	1470.38	□ H16-C13-C15+□ H18-C14-C17+□ H19-C17-C15 (24)
21	1412	1470.83		□□□□-C22 (30)
22	1398	1456.25	1449.07	□ H27-C10-C8+□ H28-C8-C10 (40)
23	1352	1408.33		□□□□-C12 (27)
24	1352	1408.33		□ C11-C12-C14+□ C12-C14-C17+□ C13-C15-C17+□ C15-C17-C14 (14)
25	1294	1347.92	1341.16	□□C12-C14+□□C13-C15+□□C15-C17+ □ C17-C14 (38)
26	1271	1323.96		□ H26-C9-O7 (31)
27	1214	1264.58	1275.44	□□C12-C14+□□C13-C15+□□C15-C17+ □ C17-C14 (31)
28	1211	1261.46		□ H16-C13-C15-C17+□ H18-C14-C17-C15+□ H19-C17-C15-C13 (31)
29	1211	1261.46	1241.67	□ C6-C1-O2-C3+□ C13-C15-C17-C14+□ C15-C17-C14-C12 (19)



30	1181	1230.21		<input type="checkbox"/> H16-C13-C15-C17+ <input type="checkbox"/> H18-C14-C17-C15+ <input type="checkbox"/> H19-C17-C15-C13 (62)
31	1171	1219.79		<input type="checkbox"/> <input type="checkbox"/> O2-C1+ <input type="checkbox"/> <input type="checkbox"/> O2-C3+ <input type="checkbox"/> <input type="checkbox"/> O7-C6+ <input type="checkbox"/> O7-C9 (39)
32	1171	1219.79		<input type="checkbox"/> N4-C1-O2+ <input type="checkbox"/> N5-C3-O2 (18)
33	1154	1202.08		<input type="checkbox"/> H26-C9-O7-C6+ <input type="checkbox"/> H27-C10-C9-C7+ <input type="checkbox"/> H28-C8-C10-C9 (71)
34	1142	1189.58	1153.52	<input type="checkbox"/> <input type="checkbox"/> O2-C1+ <input type="checkbox"/> <input type="checkbox"/> O2-C3+ <input type="checkbox"/> <input type="checkbox"/> O7-C6+ <input type="checkbox"/> O7-C9 (34)
35	1105	1151.04		<input type="checkbox"/> C8-C6-O7+ <input type="checkbox"/> C10-C9-O7 (45)
36	1076	1120.83		<input type="checkbox"/> H26-C9-O7-C6+ <input type="checkbox"/> H27-C10-C9-C7+ <input type="checkbox"/> H28-C8-C10-C9 (74)
37	1074	1118.75	1108.86	<input type="checkbox"/> C1-O2-C3+ <input type="checkbox"/> O2-C3-C11+ <input type="checkbox"/> O7-C6-C11+ <input type="checkbox"/> C9-O7-C6 (18)
38	1050	1093.75	1080.37	<input type="checkbox"/> <input type="checkbox"/> O2-C1+ <input type="checkbox"/> <input type="checkbox"/> O2-C3+ <input type="checkbox"/> <input type="checkbox"/> O7-C6+ <input type="checkbox"/> O7-C9 (42)
39	1025	1067.71	1057.28	<input type="checkbox"/> H16-C13-C15-C17+ <input type="checkbox"/> H18-C14-C17-C15+ <input type="checkbox"/> H19-C17-C15-C13 (59)
40	1006	1047.92		<input type="checkbox"/> C8-C6-O7+ <input type="checkbox"/> C10-C9-O7 (50)
41	991	1032.29	1016.25	<input type="checkbox"/> C1-O2-C3+ <input type="checkbox"/> O2-C3-C11+ <input type="checkbox"/> O7-C6-C11+ <input type="checkbox"/> C9-O7-C6 (19)
42	970	1010.42		<input type="checkbox"/> <input type="checkbox"/> O2-C1+ <input type="checkbox"/> <input type="checkbox"/> O2-C3+ <input type="checkbox"/> <input type="checkbox"/> O7-C6+ <input type="checkbox"/> O7-C9 (10)
43	970	1010.42		<input type="checkbox"/> N4-C1-O2+ <input type="checkbox"/> N5-C3-O2 (43)
44	923	961.46	970.38	<input type="checkbox"/> C3-C12-C13-C11 (13)
45	910	947.92		<input type="checkbox"/> H26-C9-O7-C6+ <input type="checkbox"/> H27-C10-C9-C7+ <input type="checkbox"/> H28-C8-C10-C9 (90)
46	885	921.88	900.71	<input type="checkbox"/> <input type="checkbox"/> F23-C22+ <input type="checkbox"/> <input type="checkbox"/> F24-C22+ <input type="checkbox"/> <input type="checkbox"/> F25-C22 (23)
47	865	901.04	883.65	<input type="checkbox"/> N4-C6-O2-C1+ <input type="checkbox"/> N5-C11-O2-C3 (51)
48	809	842.71	862.40	<input type="checkbox"/> N4-C6-O2-C1+ <input type="checkbox"/> N5-C11-O2-C3 (33)
49	792	825.00	825.35	<input type="checkbox"/> C11-C12-C14+ <input type="checkbox"/> C12-C14-C17+ <input type="checkbox"/> C13-C15-C17+ <input type="checkbox"/> C15-C17-C14 (24)
50	713	742.71	744.96	<input type="checkbox"/> F23-C22-F25+ <input type="checkbox"/> F24-C22-F23+ <input type="checkbox"/> F25-C22-F24 (36)
51	673	701.04	727.01	<input type="checkbox"/> C10-C9-O7-C6+ <input type="checkbox"/> C11-C12-C14-C17 (30)
52	673	701.04		<input type="checkbox"/> C10-C9-O7-C6+ <input type="checkbox"/> C11-C12-C14-C17 (25)
53	669	696.88	660.12	<input type="checkbox"/> F24-O21-F23-C22+ <input type="checkbox"/> F25-O21-F24-C22 (32)
54	661	688.54	587.26	<input type="checkbox"/> F24-O21-F23-C22+ <input type="checkbox"/> F25-O21-F24-C22 (21)
55	485	505.21	541.31	<input type="checkbox"/> <input type="checkbox"/> C3-C11+ <input type="checkbox"/> <input type="checkbox"/> C6-C1 (16)
56	466	485.42		<input type="checkbox"/> F23-C22-F25+ <input type="checkbox"/> F24-C22-F23+ <input type="checkbox"/> F25-C22-F24 (36)
57	429	446.88		<input type="checkbox"/> F23-C22-F25+ <input type="checkbox"/> F24-C22-F23+ <input type="checkbox"/> F25-C22-F24 (20)
58	417	434.38		<input type="checkbox"/> C6-C1-O2-C3+ <input type="checkbox"/> C13-C15-C17-C14+ <input type="checkbox"/> C15-C17-C14-C12 (18)
59	326	339.58		<input type="checkbox"/> <input type="checkbox"/> C3-C11+ <input type="checkbox"/> <input type="checkbox"/> C6-C1 (15)
60	326	339.58		<input type="checkbox"/> C1-O2-C3+ <input type="checkbox"/> O2-C3-C11+ <input type="checkbox"/> O7-C6-C11+ <input type="checkbox"/> C9-O7-C6 (15)
61	326	339.58		<input type="checkbox"/> Br20-C15-C17 (26)
62	282	293.75		<input type="checkbox"/> C1-O2-C3-C11+ <input type="checkbox"/> O2-C3-C11-C12+ <input type="checkbox"/> O7-C6-C1-O2+ <input type="checkbox"/> C9-O7-C6-C8 (22)
63	270	281.25		<input type="checkbox"/> <input type="checkbox"/> Br20-C15 (16)
64	270	281.25		<input type="checkbox"/> C11-C12-C14+ <input type="checkbox"/> C12-C14-C17+ <input type="checkbox"/> C13-C15-C17+ <input type="checkbox"/> C15-C17-C14 (14)
65	268	279.17		<input type="checkbox"/> O21-C12-C14 (23)
66	163	169.79		<input type="checkbox"/> C22-O21-C12 (34)
67	163	169.79		<input type="checkbox"/> Br20-C13-C17-C15 (16)
68	140	145.83		<input type="checkbox"/> C6-C1-O2-C3+ <input type="checkbox"/> C13-C15-C17-C14+ <input type="checkbox"/> C15-C17-C14-C12 (18)

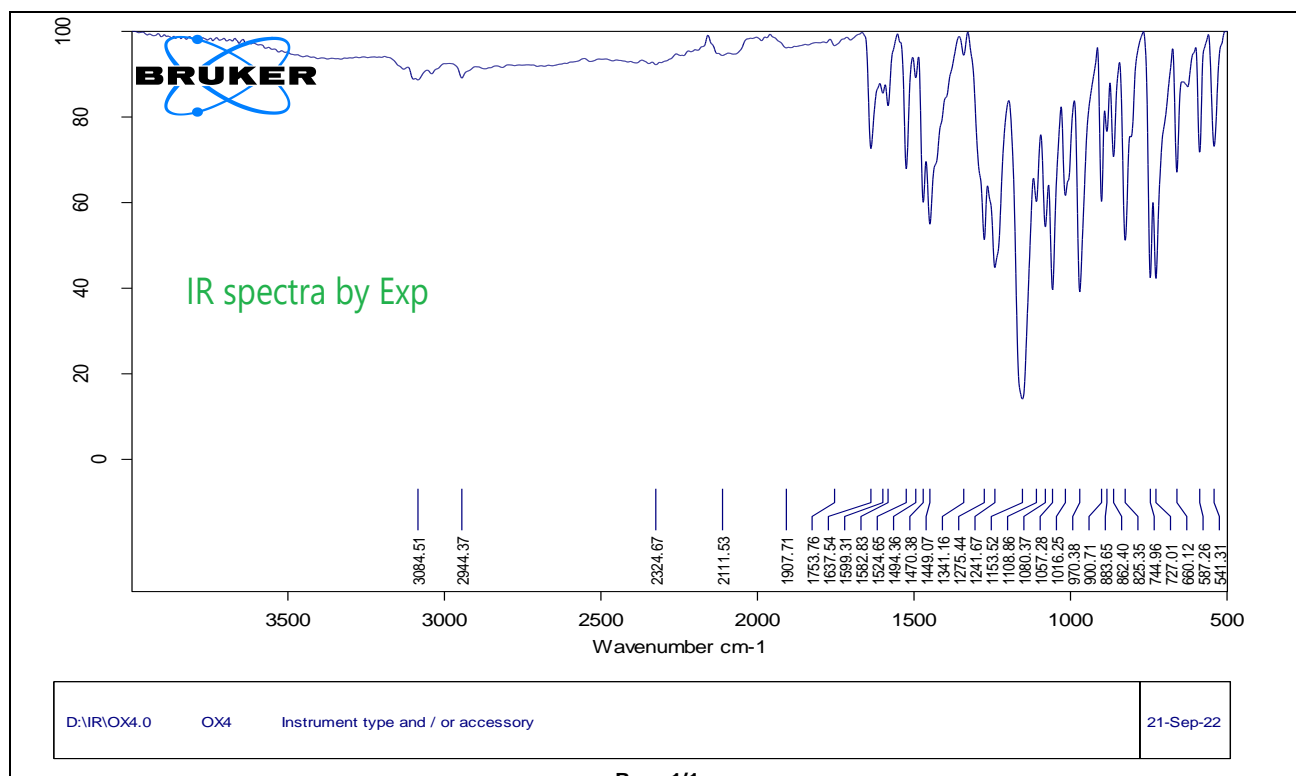


69	140	145.83		□ C8-C1-O7-C6 (23)
70	126	131.25		□ C6-C1-O2 (22)
71	120	125.00		□ C1-O2-C3-C11+□ O2-C3-C11-C12+□ O7-C6-C1-O2+□ C9-O7-C6-C8 (31)
72	85	88.54		□ C1-O2-C3-C11+□ O2-C3-C11-C12+□ O7-C6-C1-O2+□ C9-O7-C6-C8 (34)
73	78	81.25		□ C3-C11-C13 (18)
74	62	64.58		□ C1-O2-C3+□ O2-C3-C11+□ O7-C6-C11+□ C9-O7-C6 (12)
75	62	64.58		□ F23-C22-O21-C12 (45)
76	61	63.54		□ O21-C11-C14-C12 (24)
77	49	51.04		□ C22-O21-C12-C11 (47)
78	27	28.13		□ C1-O2-C3-C11+□ O2-C3-C11-C12+□ O7-C6-C1-O2+□ C9-O7-C6-C8 (37)

3.5.2 Oxadiazole ring vibration:

Usually, C-H modes of vibrations [24] in benzene ring lie in the range of $3100-3000\text{ cm}^{-1}$ without any deviation and the intensity of these peaks will form an umbrella pattern with weak to medium level peaks, which happens always when the molecule has more than

three C-H bonds. In this present study, there are three C-H bonds in benzene ring and was manifested at $3241, 3237$ and 3224 cm^{-1} . These values are elevated from the cited range, which indicate the varied conjugation in the benzene ring. Similarly, C-H in plane bending [14] is expected in the region of $1341-1100\text{ cm}^{-1}$.



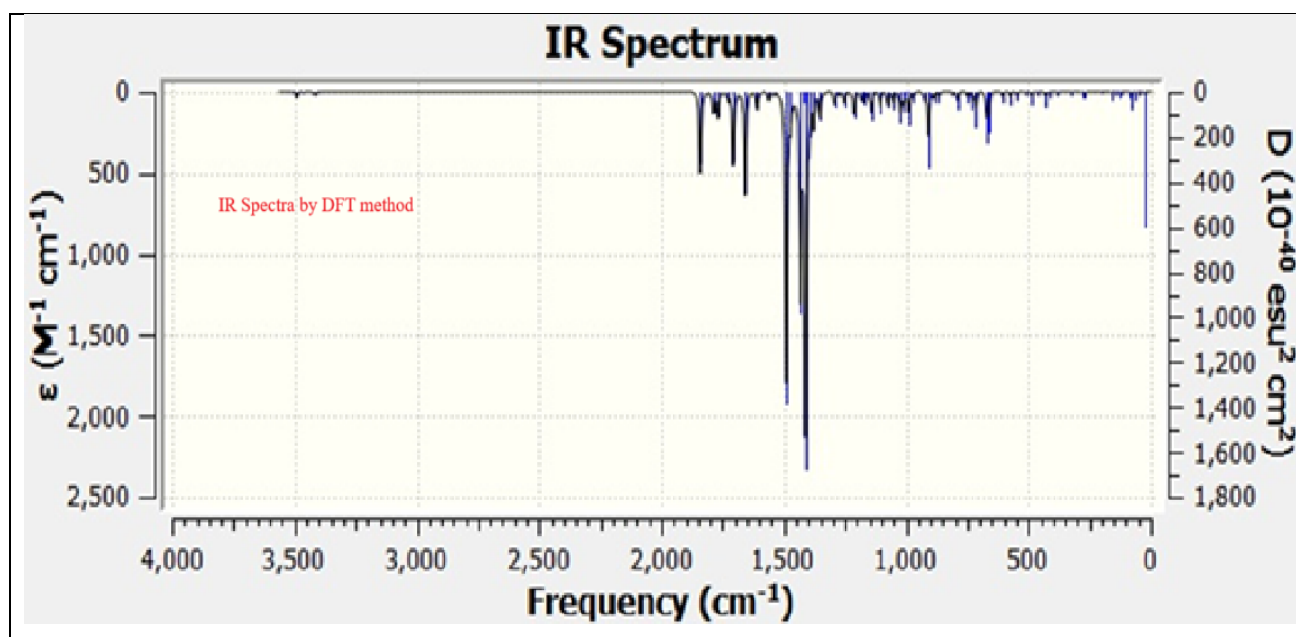


Figure 4: IR spectra of 5-(furan-2-yl)-5-(5-bromo-2-(trifluoromethoxy)phenyl) 1,3,4-oxadiazole by Experimental and DFT method

3.5.3 Trifluoro methyl group vibration:

In this group of vibration, the C-F extending vibrations are assigned in the area of 1250-900 cm^{-1} and their corresponding computed vibrational frequencies are analyzed at 1241 as well as 900 cm^{-1} respectively. Finally, it is cleared that vibrational modes were affected due to the presence of furan and oxadiazole ring with those bonds and the physical and chemical properties of the affected elements were changed according to the dominant group [14].

3.6 NMR Analysis

Table 5 lists the spectrum values for ^1H and ^{13}C and its theoretical values are given in **Table 6**. The aromatic area of present compound is 7.98 to 9.64 ppm, when aromatic protons are detected. Due to Br's deshielding of the nucleus and the signal downfield, the H19 signal is detected at 9.64 ppm. Thirteen distinct signals are displayed by ^{13}C NMR, signifying the presence of various carbon types. The π -conjugation from O23 causes the C14 and C17 signals to shift upfield, indicating that the electron-donating action of oxygen is more prominent through conjugation than the electron-withdrawing effect because of electronegativity.

Because the furan ring has a drawing effect of 70, the carbon atoms C9 and C7 also needed a high field to resonate. The three fluorine atoms' electron-withdrawing action shifts the C26 signal downfield. The downfield shift of the C1 and C3 signals, which are measured at 152 and 154 ppm, respectively, indicates the presence of the electron withdrawing effect of O2, N4, and N5. [14]. Both experimental and DFT predicted ^1H and ^{13}C NMR spectra are given in **Figure 5** and **Figure 6** respectively.

Table 5: The experimental chemical shift value of 2-(5-bromo-2-(trifluoromethoxy)phenyl)-5-(furan-2-yl)-1,3,4-oxadiazole

Atom	^{13}C NMR value (Exp) δ_{ppm}	Position of hydrogen atom	^1H NMR value (Exp) δ_{ppm}
C3	166.23	H16	8.273
C1	152.74	H26	7.718
C9	149.42	H28	7.167
C6	140.74	H19	7.121
C12	132.77	H18	7.017

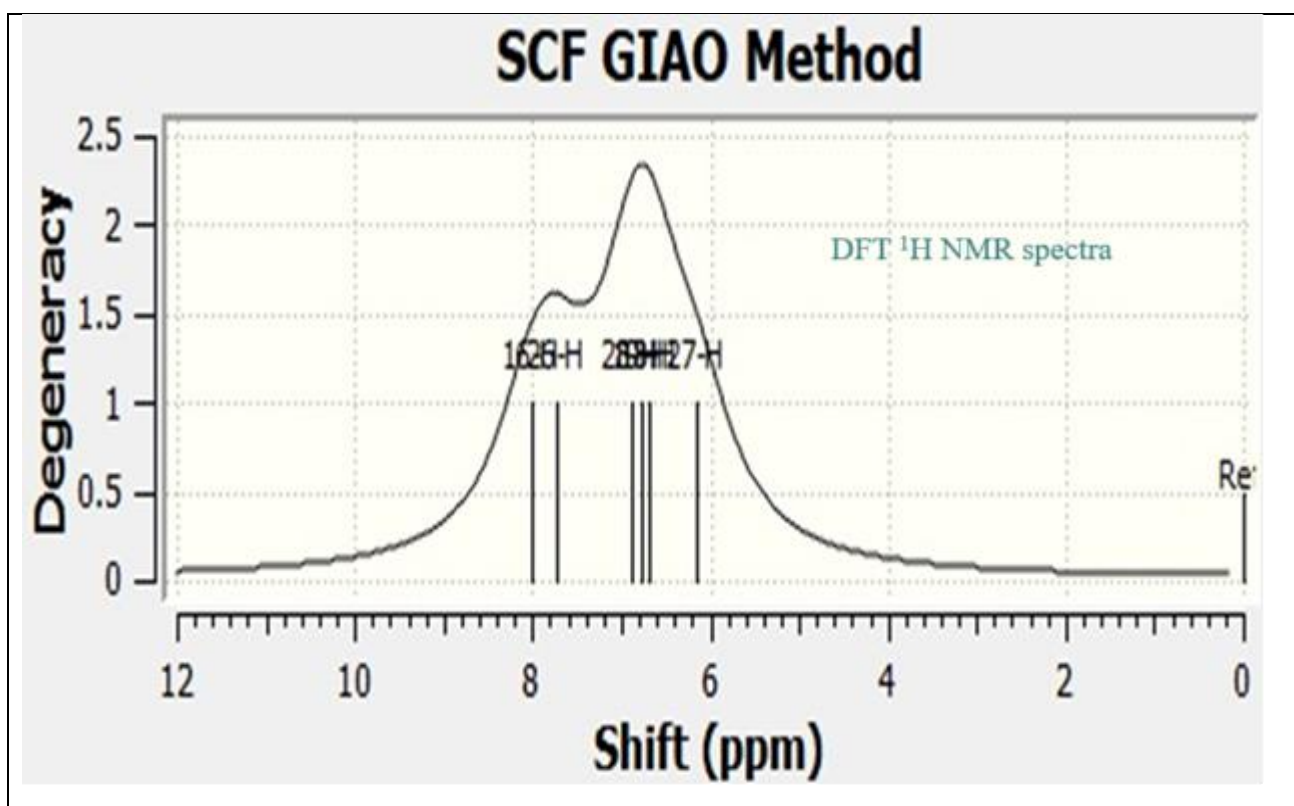
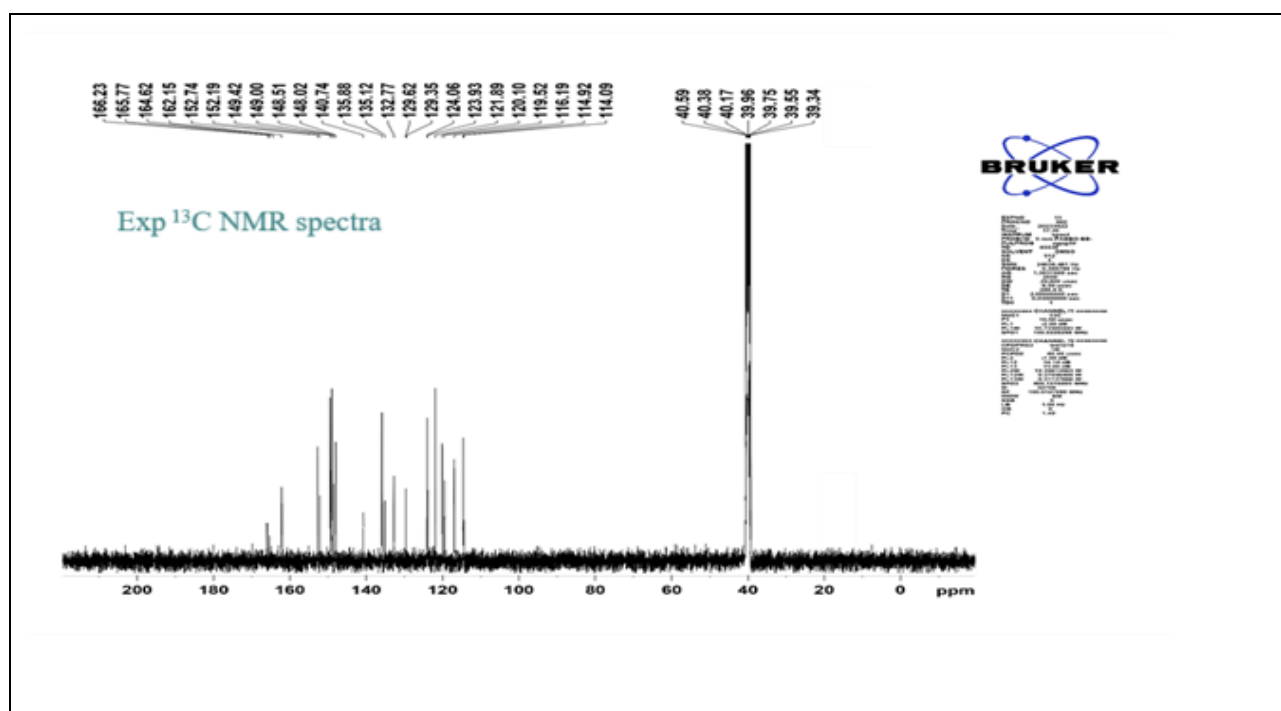


Figure 5: Experimental and DFT method ¹H NMR spectra of 2-(5-bromo-2-(trifluoromethoxy)phenyl)-5-(furan-2-yl)-1,3,4-oxadiazole



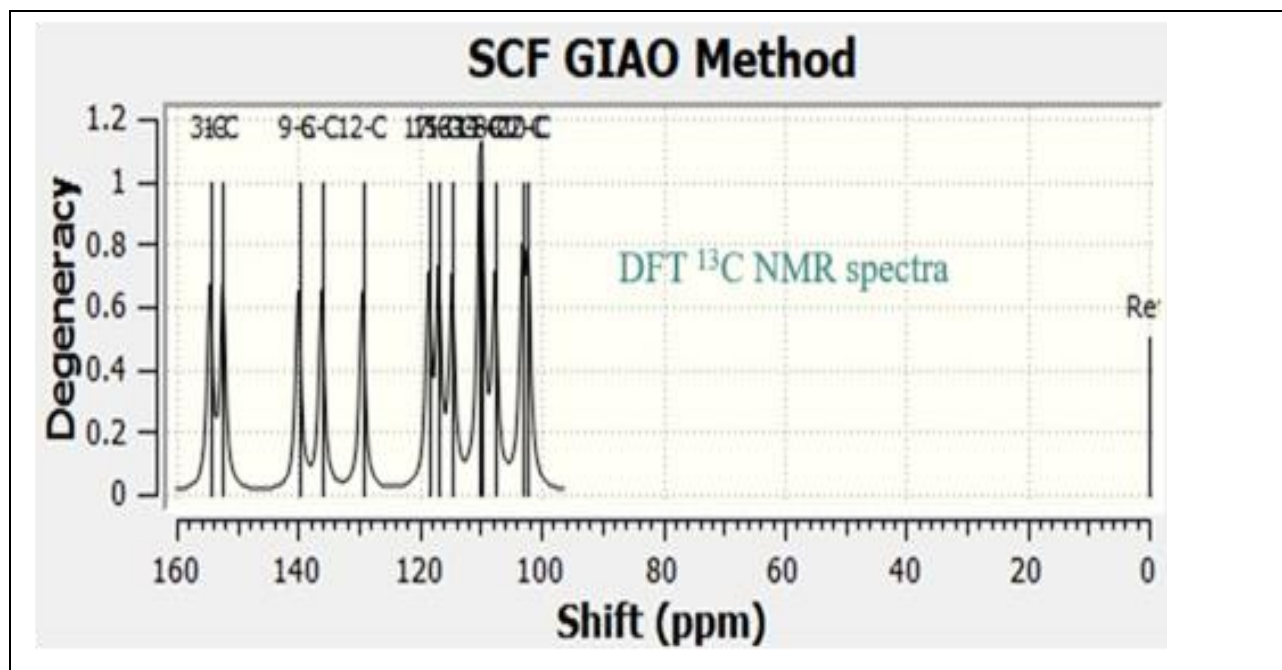


Figure 5: Experimental and DFT method ^{13}C NMR spectra of 2-(5-bromo-2-(trifluoromethoxy)phenyl)-5-(furan-2-yl)-1,3,4-oxadiazole

3.7 Mulliken population analysis :

The Mulliken charge, which measures how the electronic pattern changed upon atomic displacement, is closely linked to the aberrational properties of the molecule and, as a result, to the chemical bonds that are seen in the molecule [27, 28]. It attracts the electronic structure, polarizability, dipole moment, as well as other characteristics of molecular systems. The molecule's Mulliken as well as natural charge segregation are computed on B3LYP levels using various basis sets and are shown in the **Table 7**.

Table 7. Mulliken atomic charge of 2-(5-bromo-2-(trifluoromethoxy)phenyl)-5-(furan-2-yl)-1,3,4-oxadiazole

Atom	Charge (a.u)	Atom	Charge (a.u)
C1	0.7049	C15	-0.404
O2	-0.6979	H16	0.32585
C3	0.82795	C17	-0.1708
N4	-0.4284	H18	0.29568

N5	-0.4458	H19	0.28808
C6	0.32344	Br20	0.24943
O7	-0.6627	O21	-0.7786
C8	-0.2394	C22	1.48832
C9	0.16053	F23	-0.3732
C10	-0.3485	F24	-0.3858
C11	-0.2136	F25	-0.3833
C12	0.37223	H26	0.28547
C13	-0.1285	H27	0.26442
C14	-0.2196	H28	0.29381

Because of the nearby carbonyl group's net atomic charge, the hydrogen atoms 26 and 28 that are joined to the carbon atoms O2, O7, and O21 in the title molecule have the highest negative charge. Because the electronegative oxygen and nitrogen atoms are bound to the corresponding C3, C23, and C34 carbon atoms, the large +ve charge of 0.715, 0.623, as well as 0.513 for C3, C22, as well as atoms is seen in **Figure 7**.

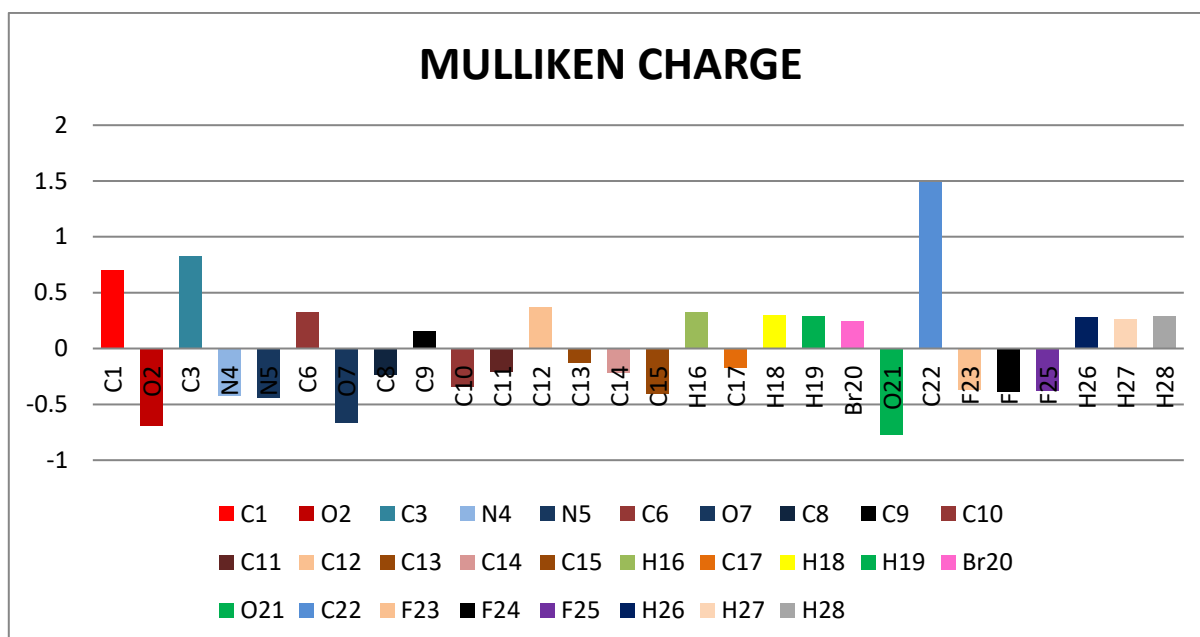


Figure 7. Column chart of Mulliken charges of 2-(5-bromo-2-(trifluoromethoxy)phenyl)-5-(furan-2-yl)-1,3,4-oxadiazole

4. Conclusion:

The synthesis and computational investigation of a novel nonlinear compound, 2-(5-bromo-2-(trifluoromethoxy)phenyl), are reported in this paper. The geometry of -5-(furan-2-yl)-1,3,4-oxadiazole, which was synthesized and its structure examined, illustrates how mesomeric impacts as well as resonance delocalization shorten the bond lengths of carbonyls. The predicted product structure and the rotational potential shifting in the ¹H and ¹³C-NMR were appropriately in agreement. FT-IR and FT-Raman spectra are used to analyze the vibrational potential transfer inside the molecule; the results of these spectra are consistent with one another and may also be compared to simulated spectra. Vibrational dynamics could be ascribed and a detailed vibrational picture of this new material could be identified. The UV-visible spectrum was used to study electron transportation between different orbitals, while TD-DFT calculations were used to study optical transport. Both methods were appropriately agreed upon. The molecule's simple semiconducting nature and similar nonlinear optical properties (4.5740eV/ π - π^* transition) are shown. According to calculations, the first hyperpolarizability is 7.855X10⁻³⁰ esu, which is 21 times higher than that of urea. The molecule becomes more stable as a result of the strong hyper conjugative

interactions. This interaction is especially important for nonlinear molecules that interact through a conjugated π system and have a high intramolecular charge transfer from electron donating group to electron withdrawing group (D- π -A). The charge positions of the molecules are disclosed by the mapped surface of the molar electrostatic capacity. The presence of the carbonyl group affects additional molecular characteristics.

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