Research article

Quantum chemical determination of molecular geometries and spectral investigation of 4-ethoxy-2, 3-difluoro benzamide

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ABSTRACT

The present work reports the application of density functional theory (DFT) at B3LYP with various basis sets which provide the relationship between the structural and spectral properties of 4-ethoxy-2, 3-difluoro benzamide (4EDFB). A Complete vibrational analysis has been performed at the density functional theory (DFT) method with various basis sets in the ground state. The results of vibrational wave numbers are in good agreement with the experimental spectra (Infrared and Raman). Energy gap of the molecule is evaluated using frontier molecular orbital energies (HOMO-LUMO). The frontier energy gap value reveals the chemical reactivity and intermolecular charge transfer occur within the molecule. Global chemical descriptors provide the local and global softness and local reactivity parameters used to identify the nucleophilic and electrophilic behavior of a specific site within the compound. The dimer structure is performed to evaluate the intermolecular hydrogen bond (O–H–O). The title molecule is capable of receiving second harmonic generation (SHG) is due to high value of hyperpolarizability indicates the NLO activity of the molecule. Apart from NLO entities, aromaticity and the molecular electrostatic potential surface (MEP) explain the hydrogen bonding and provide the reactive behavior of the molecule. The Mulliken population analysis leads to redistribution of electron density in the ring.

1. Introduction

Benzamide derivatives [1, 2] have great pharmaceutical utility, particularly in the treatment of diabetics and show significant antibacterial, antihelmintic, anti-inflammatory, antimalarial, antitumor and antiallergic activities as well as used in the preparation of an aromatic ligand. Recently, for Tri-fluoro methyl containing 4-(2-Pyrimidinylamino) benzamides derivatives were evaluated the more potent Hedge hog (Hh) signaling inhibitory activity and Hh signaling pathway which have potential for treatment of many human tumors, such as medulloblastoma ovarian, prostate leukemia lung, pancreatic melanoma, glioblastoma and basal cell carcinoma (BCC). It has been proved that, a range of synthesized di- and triarylbenzamide compounds were tested for their antiproliferative activity as well as their DNA binding activity and 4-Benzoylaminocarbonyl-4-(prop-2-yn-1-yl) benzamides are act as novel microRNA-21 (miRNAs) inhibitors for breast cancer. For instance, miR-21 inhibition was alone to suppress tumor cell proliferation in-vitro and could enhance the several types of cancer cells to taxol and much help in chemotherapy and hence it is considered as therapeutic target in human cancer treatment [3]. The novel heteroaromatic-containing benzamide derivatives can be used as a glucokinase activator (GKA) for the treatment of type 2 diabetic mellitus [4, 5, 6]. SOLIAN (4-amino-N-(1-ethyl pyroldin-2-yl) methyl)-5-ethyl sulphonyl-2-methoxy benzamide) is a benzamide derivative chemically related to sulpiride which shows antischizophrenic and antidysthymic drug for the treatment of dysthymic disorders as well as for the determination of amisulphide by HPLC in human plasma analysis with UV absorbance detection [7, 8]. The various halogenated benzamide derivatives used as radiotracers, which played in diagnosing malfunction in dopaminergic neurotransmission [9] have been implicated in a variety of neuropsychiatric disease such as parkinson’s disease and drug abuse. Yifan Jin et.al investigated the reaction mechanisms of alkaline hydrolysis of N-(2-methoxyphenyl) benzamide which is used in the chemical industry [10]. Anil Kumar et.al [11] studied the antimicrobial and QSAR studies of substituted benzamides.

Thus, owing to the extensive medical significance of benzamide, this present work decided to interpret the vibrational analysis of 4-ethoxy-2, 3-difluoro benzamide (4EDFB) compound. Recently the vibrational and

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spectral investigations of 2-fluoro benzamide and 2,6- dichloro benzamide were discussed by using DFT studies [12, 13]. Therefore, In the present investigation, results on the structural and quantum chemical computations of title compound 4-ethoxy-2,3-difluoro benzamide (4EDFB) is reported. In recent years, the interpretations of vibrational and structural characteristics using density functional theory computations have been widely increasing in the pharmaceutical field. Because of this considerations, DFT computations along with vibrational spectroscopic investigations will be employed to determine the complete vibrational assignment on 4-ethoxy-2,3-difluoro benzamide(4EDFB). Additionally, optimized geometrical parameters, HOMA index, Molecular electrostatic potential, Mulliken charges, Fukui functions, NLO, HOMO-LUMO energy gap and the different electronic properties from the frontier orbitals and hydrogen bond of the little molecule have been performed by using DFT/B3LYP with 6-31+G (d,p) and 6-311++G (d,p) basis sets.

2. Methods

2.1. Experimental

The 4-ethoxy-2, 3-difluoro benzamide (4EDFB) with greater purity was purchased from chemical company and directly used for the spectral measurements without further purification. The FT-IR spectrum was recorded by Nd-YAG laser between 4000 and 400 cm⁻¹ and the FT-Raman spectrum was collected using IFS- 66V model interferometer as excitation wavelength in the range of 3500–50 cm⁻¹.

2.2. Quantum chemical methods

To determine the minimum energy corresponding to most
with selected dihedral angle C4–C17–H18 was performed using B3LYP exchange correlation function with 6-31+G (d,p) basis set. Subsequently, structural parameters corresponding to the optimized conformation of 4EDFB, the potential energy surface (PES) scan along with selected dihedral angle C4–C17–H18 was performed using B3LYP exchange correlation function with 6-31+G (d,p) basis set. The results are depicted in Fig. 2. The most minimum energy of the present compound is predicted to be -0.243767 a. u at B3LYP/6-31+G (d,p).

### 3. Results and discussions

#### 3.1. Potential energy scan

In accordance with the atom numbering scheme of title molecule is given in Fig. 1. The theoretically computed structural parameters are listed in Table 1. In order to obtain the most stable energy of 4EDFB, the detailed potential energy scan profile is performed [16] by choosing the angle C4–C10–C17–H18 that varies in every 60 steps for the angle 180° to get the stable geometry of the molecule and the results are depicted in Fig. 2. The most minimum energy of the present compound is predicted to be -0.243767 a. u at B3LYP/6-31+G (d,p).

### 3.2. Molecular geometry

The molecule consisting different functions substitutes to the benzene ring causes some changes in structural and electronic properties. From geometry and harmonic frequencies for PES minima were found to obtain zero point vibration energy (ZPE) using Gaussian 09W Program at B3LYP with 6-31+G (d,p) and 6–311++G (d,p) basis sets [14]. In recent years B3LYP approach used extensively which gives reliable results of molecules with very satisfactory geometries. The scaled frequencies obtained by the theoretical calculations on the basis of the potential energy distribution (PED) has been done with the MOLVIB program (version 7.0-G77) written by sundius [15] and these normal modes were compared with the experimental FT-IR and Raman spectra of the title compound. In order to predict the stability of the molecule, HOMO-LUMO analysis were examined and the global hardness(\(\eta\)), Chemical potential (\(\mu\)), electron negativity (\(\chi\)) have been computed using the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). In order to find the Non Linear optical activity of the molecule (NLO), the dipole moment, polarizability, first and second order hyperpolarizabilities were obtained for future studies. To determine the reactive behavior of the molecule the fukui functions were also reported. Molecular electrostatic potential surface analysis used for predicate reactive sites and the positive and negative regions of MEP are related to nucleophilic and electrophilic reactivity. Furthermore, aromaticity of molecule, intermolecular interaction and using Mulliken population analysis, the net charges of the title molecule can be evaluated.

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**Table 1 (continued)**

| Parameters | B3LYP Method |
|------------|--------------|
|            | 6-31+G (d,p) | 6-311++G (d,p) |
| C6-C1-C7-O13 | 0.617 | 0.16 |
| C6-C1-C7-N14 | -179.4 | -180 |
| C1-C2-C3-C4 | -1.04 | -1.07 |
| C1-C2-C3-F9 | 178.5 | 178.3 |
| F8-C2-C3-C4 | 179.6 | 179.6 |
| F8-C2-C3-F9 | -0.78 | -1.01 |
| C2-C3-C4-C5 | 1.16 | 1.27 |
| C2-C3-C4-O10 | 178.0 | 180.0 |
| F9-C3-C4-C5 | -178.4 | -178.1 |
| F9-C3-C4-O10 | -1.53 | -1.35 |
| C3-C4-C5-C6 | -0.49 | -0.58 |
| C3-C4-C5-H11 | 179.6 | 179.5 |
| O10-C4-C5-C6 | -177.7 | -177.6 |
| C10-C4-C5-H11 | 2.41 | 2.51 |
| C3-C4-O10-C17 | 28.7 | 31.9 |
| C5-C4-O10-C17 | -154.4 | -151.4 |
| C4-C5-C6-C1 | -0.36 | -0.36 |
| C4-C5-C6-H12 | -179.8 | -179.7 |
| H11-C5-C6-C1 | 179.6 | 179.5 |
| H11-C5-C6-H12 | 0.14 | 0.15 |
| C1-C7-N14-H15 | 179.6 | 179.3 |
| C1-C7-N14-H16 | 0.60 | 1.33 |
| O13-C7-N14-H15 | -0.43 | -0.9 |
| O13-C7-N14-H16 | -179.4 | -178.8 |
| C4-C10-C17-H18 | -61.7 | -62.8 |
| C4-C10-C17-H19 | -177.1 | -178.2 |
| C4-C10-C17-C20 | 63.7 | 62.5 |
| O10-C17-C20-H21 | 59.4 | 55.7 |
| O10-C17-C20-H22 | 174.7 | 175.07 |
| O10-C17-C20-H23 | -66.2 | -65.9 |
| H18-C17-C20-H21 | 179.9 | -179.9 |
| H18-C17-C20-H22 | -60.8 | -60.5 |
| H18-C17-C20-H23 | 58.3 | 58.6 |
| H19-C17-C20-H21 | -58.9 | -58.7 |
| H19-C17-C20-H22 | 60.4 | 60.6 |
| H19-C17-C20-H23 | 179.5 | 179.7 |

For numbering of atoms, refer Fig. 1.

\* Experimental data from (12).

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**Fig. 2.** Scanning profile of 4-ethoxy-2,3-difuoro benzamide.
### Table 2
Vibrational assignments of 4 - Ethoxy-2,3-difluoro benzamide along with Observed FT-IR and FT-Raman and calculated (unscaled and scaled) frequencies (cm\(^{-1}\)) using B3LYP method with 6-31+G (d,p) and 6-311++G (d,p) basis sets.

| S.No | C1 Symmetry | FT-IR: Observed frequencies cm\(^{-1}\) | FT Raman: Observed frequencies cm\(^{-1}\) | B3LYP/6-31+G (d,p): Calculated frequencies cm\(^{-1}\) | B3LYP/6-311++G (d,p): Calculated frequencies cm\(^{-1}\) | Assignment with TED % |
|------|-------------|------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|----------------------|
|      |             | FT-IR                                    | FT Raman                                     | Unscaled                                      | Scaled                                        | Unscaled                                  |
|      |             |                                          |                                               |                                               |                                               | Scaled                                    |
| 1    | A           | 3409                                     | -                                             | 3748                                          | 3414                                          | 3731                                    |
| 2    | A           | 3200                                     | -                                             | 3606                                          | 3205                                          | 3598                                    |
| 3    | A           | -                                        | 3125                                          | 3230                                          | 3131                                          | 3211                                    |
| 4    | -           | 3075                                     | -                                             | 3216                                          | 3079                                          | 3197                                    |
| 5    | A           | 3040                                     | -                                             | 3148                                          | 3045                                          | 3131                                    |
| 6    | A           | -                                        | 2983                                          | 3124                                          | 2987                                          | 3102                                    |
| 7    | A           | 2961                                     | -                                             | 3120                                          | 2966                                          | 3102                                    |
| 8    | A           | -                                        | 2933                                          | 3092                                          | 2937                                          | 3079                                    |
| 9    | A           | -                                        | 2883                                          | 3049                                          | 2888                                          | 3035                                    |
| 10   | A           | 1734                                     | -                                             | 1743                                          | 1739                                          | 1736                                    |
| 11   | A           | 1654                                     | -                                             | 1666                                          | 1659                                          | 1658                                    |
| 12   | A           | 1641                                     | -                                             | 1623                                          | 1648                                          | 1621                                    |
| 13   | A           | -                                        | 1629                                          | 1604                                          | 1634                                          | 1598                                    |
| 14   | A           | -                                        | 1603                                          | 1537                                          | 1607                                          | 1530                                    |
| 15   | A           | -                                        | 1588                                          | 1516                                          | 1595                                          | 1513                                    |
| 16   | A           | 1573                                     | -                                             | 1503                                          | 1581                                          | 1497                                    |
| 17   | A           | 1520                                     | 1526                                          | 1491                                          | 1529                                          | 1487                                    |
| 18   | A           | 1467                                     | 1462                                          | 1484                                          | 1466                                          | 1477                                    |
| 19   | A           | -                                        | 1436                                          | 1425                                          | 1440                                          | 1432                                    |
| 20   | A           | -                                        | 1423                                          | 1406                                          | 1431                                          | 1404                                    |
| 21   | A           | 1414                                     | -                                             | 1376                                          | 1419                                          | 1365                                    |
| 22   | A           | -                                        | 1398                                          | 1366                                          | 1403                                          | 1353                                    |
| 23   | A           | 1361                                     | -                                             | 1320                                          | 1367                                          | 1321                                    |
| 24   | A           | 1334                                     | -                                             | 1302                                          | 1338                                          | 1292                                    |
| 25   | A           | -                                        | 1308                                          | 1233                                          | 1315                                          | 1229                                    |
| 26   | A           | -                                        | 1294                                          | 1223                                          | 1298                                          | 1217                                    |
| 27   | A           | -                                        | 1282                                          | 1191                                          | 1280                                          | 1188                                    |
| 28   | A           | 1227                                     | -                                             | 1166                                          | 1234                                          | 1165                                    |
| 29   | A           | -                                        | 1218                                          | 1109                                          | 1225                                          | 1107                                    |
| 30   | A           | 1173                                     | 1167                                          | 1100                                          | 1177                                          | 1099                                    |
| 31   | A           | -                                        | 1129                                          | 1071                                          | 1133                                          | 1064                                    |
| 32   | A           | -                                        | 1116                                          | 1017                                          | 1119                                          | 1013                                    |
| 33   | A           | 1107                                     | -                                             | 989                                           | 1116                                          | 991                                     |
| 34   | A           | 1084                                     | -                                             | 921                                           | 1088                                          | 918                                     |
| 35   | A           | -                                        | 1065                                          | 883                                           | 1068                                          | 882                                     |
| 36   | A           | 1027                                     | -                                             | 852                                           | 1030                                          | 854                                     |
| 37   | A           | -                                        | 936                                           | 815                                           | 940                                          | 817                                     |
| 38   | A           | 867                                      | 872                                           | 768                                           | 874                                          | 774                                     |
| 39   | A           | 808                                      | -                                             | 729                                           | 808                                          | 731                                     |
| 40   | A           | 747                                      | 744                                           | 694                                           | 753                                          | 708                                     |
| 41   | A           | 720                                      | 718                                           | 682                                           | 727                                          | 682                                     |
| 42   | A           | 654                                      | -                                             | 627                                           | 661                                          | 628                                     |
| 43   | A           | -                                        | 642                                           | 619                                           | 649                                          | 620                                     |
| 44   | A           | 627                                      | -                                             | 578                                           | 635                                          | 577                                     |
| 45   | A           | -                                        | 603                                           | 550                                           | 611                                          | 551                                     |
| 46   | A           | 587                                      | 590                                           | 531                                           | 597                                          | 532                                     |
| 47   | A           | -                                        | 539                                           | 508                                           | 546                                          | 503                                     |
| 48   | A           | -                                        | 514                                           | 458                                           | 523                                          | 459                                     |
| 49   | A           | 507                                      | -                                             | 401                                           | 516                                          | 402                                     |
| 50   | A           | -                                        | 429                                           | 367                                           | 435                                          | 367                                     |
| 51   | A           | -                                        | 386                                           | 329                                           | 385                                          | 330                                     |
| 52   | A           | -                                        | 372                                           | 314                                           | 382                                          | 315                                     |
| 53   | A           | -                                        | 344                                           | 297                                           | 353                                          | 297                                     |
| 54   | A           | -                                        | 315                                           | 292                                           | 324                                          | 283                                     |
| 55   | A           | -                                        | 230                                           | 274                                           | 239                                          | 270                                     |
| 56   | A           | -                                        | 188                                           | 266                                           | 197                                          | 262                                     |
| 57   | A           | -                                        | 116                                           | 215                                           | -                                             | 213                                     |
| 58   | A           | -                                        | -                                             | 178                                           | -                                             | 178                                     |
| 59   | A           | -                                        | 102                                           | 146                                           | 111                                          | 144                                     |
| 60   | A           | -                                        | 88                                            | 104                                           | 97                                            | 103                                     |
| 61   | A           | -                                        | 60                                            | 71                                            | 65                                            | 65                                     |
| 62   | A           | 44                                        | 51                                            | 44                                            | 55                                            | 54                                     |
| 63   | A           | 22                                        | 19                                            | 34                                            | 21                                            | 35                                     |

Abbreviations: R – ring; ν - stretching; b-in- plane bending; α – out-of-plane bending; τ – torsion; ss-symmetric stretching; ass-asymmetric stretching; ips-in-plane stretching; symd – symmetric deformation; asynd – antisymmetric deformation; trgd – trigonal deformation; sciss: scissoring; rock: rocking; wag: wagging & twist: twisting.
the computed values, the C–C aromatic distances within the ring are found to be equal around 1.40Å (C1–C2 = C2–C3 = C5–C6 = C1–C6 = C3–C4 = C4–C5) which indicates the indistinctness between the single and double bond due to the π conjugation of electrons [17]. In the case of benzamide, the value of C–C bond length is (1.51Å) (C1–C7 = C17–C20) dramatically increases when compared to C–C bond length of the ring is due to no delocalization of electrons. The bond length of functional substituent of benzamide such as methyl (C–H = 1.01Å), methylene (C–H = 1.01Å) and amide (N–H = 1.01Å) groups are identical which shows the symmetrical arrangement of atoms. The calculated C–N (1.36Å) bond length coincides with the actual bond length. Among the C–O bond, the bond length of C1–O10 (1.35Å) is shorter due to presenting single and double bond between the carbon and oxygen atoms elucidating the more electrons are participated in the double bond [18]. In the benzene ring, endocyclic C–C bond angles are found to be around 120°, among these, a small reduction in two angles (C2–C1–C6 = 116°.0 and C3–C4–C5 = 117°.1) and small increases in four angles (C1–C2–C3 = 122°.7, C2–C3–C4 = 120°.8, C4–C5–C6 = 121°.3 and C1–C6–C5 = 122°.1) are observed due to the substitution in the ring which is not sharing the electrons [12]. However, the variation of the bond angle depends on the factors such as lone pair of electrons in the central atom, size of ligand atoms, electronegativity and hybridization of the central atom. For example, the bond angle decreases when the size of the central atom increases and the bond angle increases when the size of ligand atom increases [19]. The bond angle decreases due to the presence of lone pairs which causes more repulsion on the bond pairs tend to come closer. It is evident that the bond angle C1–C7–O13 (120°.3) is little greater than the bond angle C1–C7–N14 (118°.1) that shows the oxygen being more electronegative than nitrogen.

From the optimized structural parameters, it is observed that the most of the bond lengths and bond angles are consistent with the earlier reports [12, 13] and also the optimized bond lengths are coincide well with the bond length obtained by XRD data [12].

3.3. Spectral analysis

The title molecule is non-planar which belongs to C1 point symmetry and it consist of 23 atoms that undergoes 63 normal modes of vibrations. The detailed vibrational assignment of fundamental modes computed based on the calculated TED values along with calculated FT-IR and FT-Raman frequencies of title compound which are presented in Table 2. The experimentally recorded and the theoretical FT-IR and FT-Raman spectra of 4-ethoxy-2, 3-di-fluoro benzamide is depicted in Figs. 3 and 4.

To obtain better agreement between the calculated and experimental wave numbers the scale factors were applied and discussed below [20, 21]. The comparison of the scaled wave numbers with recorded values demonstrates that the computed at B3LYP method with 6-31+G (d, p)/6–311++G (d, p) basis sets are well consistent with the experimental spectra. The correlation graphic between theoretical and experimental wave numbers are linear which is depicted in Fig. 5 and is defined by the following expressions.

\[
\nu_{\text{Cal}} = 0.9978 \ \nu_{\text{Exp}} + 18.8819 \quad (R^2 = 0.9928) \quad \text{B3LYP/6-31+G(d,p)}
\]

\[
\nu_{\text{Cal}} = 0.9982 \ \nu_{\text{Exp}} + 8.71556 \quad (R^2 = 0.9999) \quad \text{B3LYP/6-311++G(d,p)}
\]

3.4. Molecular vibrational analysis

3.4.1. NH₂ vibration

Amide group has six normal modes viz., the two stretching vibrations are asymmetric and symmetric stretching modes and four bending
vibrations are scissoring, rocking, wagging and twisting modes. Gener-
ally asymmetric stretching vibrational mode has higher frequency than
symmetric stretching mode. Normally the NH₂ stretching frequency ap-
pears in the region 3500-3300 cm⁻¹. For in-plane- bending, the wave
numbers are appear at 1700-1600 cm⁻¹ and 1150-900 cm⁻¹ for out-of-
plane bending deformations [22]. In 2-ethylpyridine-4-carbothioamide,
the stretching modes are occurring at 3430 cm⁻¹ and 3440 cm⁻¹ in IR
and Raman spectra, respectively [23]. Wysokinski et. al. have observed
these modes at 3352/3240 cm⁻¹ in IR and 3350/3236 cm⁻¹ in Raman
spectra for 4-thiocarbamoyl pyridine [24]. Yilmaz et al have assigned the
asymmetric and symmetric stretching wave numbers at 3373 cm⁻¹ and
3265 cm⁻¹ for prothionamide [25].

In the present investigation, the title
molecule consist only one NH₂ group. The two NH₂ stretching modes
assigned at 3409 cm⁻¹ and 3200 cm⁻¹ for as asymmetric stretching and
symmetric stretching modes in the FT-IR spectrum [12]. The bending
vibrations are assigned at 1173 cm⁻¹, 1641 cm⁻¹ and 1167 cm⁻¹ to NH₂
scissoring and rocking vibrations in the FT-IR and FT- Raman spectra and
twisting and wagging modes are observed at 627 cm⁻¹ (IR) and 315 cm⁻¹
(R) respectively.

3.4.2. C–H vibrations

The aromatic compounds show that the C–H stretching wave numbers are
not affected by the nature of substituents, they commonly exhibit in the
region 3100-3000 cm⁻¹ [12,26]. The C–H stretching mode was
observed at 3107 cm⁻¹ in FT-IR and at 3070 cm⁻¹ in FT-Raman for 3,
5-difluoroaniline by Pathak et.al [34]. In the present investigation, the
C–H stretching vibrations are attributed at 3125 cm⁻¹ and 3075 cm⁻¹ of
title compound. The C–H in-plane bending vibrations lie in the region
1000- 1300 cm⁻¹ and the C–H out-of -plane bending vibrations are
expected in the frequency range 750–100 cm⁻¹ - [27]. For the title
compound, in -plane bending wave numbers are observed at 1227 cm⁻¹
in FT-IR and in Raman spectrum at 1308 cm⁻¹. The bands observed at
1107 cm⁻¹ and 1027 cm⁻¹ in the FT Raman spectra are assigned to C–H
out - of-plane bending vibration.

3.4.3. CH₂ vibrations

The vibrations of CH₂ group has six fundamental modes that can be
associated to each CH₂ group namely asymmetric stretching and sym-
metric stretching, scissoring and rocking belongs to in-plane bending
vibrations and two out-of -plane bending vibrations are twisting and
wagging. The CH₂ stretching vibration generally expected in the region
3000-2800 cm⁻¹. The asymmetric and symmetric stretching bands cor-
responding to wave numbers of methylene (CH₂) group appear normally
in the expected region 3000-2900 cm⁻¹ and 2900-2800 cm⁻¹ [28].
Ramkumaar et. al [29]. has reported the CH₂ asymmetric stretching at
2968 cm⁻¹ in FT-Raman spectrum. CH₂ scissoring and wagging modes
are attributed in the region at 1651 cm⁻¹ and 1465 cm⁻¹ in FT-IR spec-
trum. Vesna et.al [30]. assigned the bands at 2978 and 2806 cm⁻¹ to
methylene asymmetric and symmetric stretching vibrations. For 4EDFB,
CH₂ asymmetric and symmetric stretching vibrations assigned at 2933
and 2883 cm⁻¹ in FT-Raman spectrum. The bending vibrations of
CH₂ scissoring, rocking, wagging and twisting modes are appear in the
expected frequency region 1500-800 cm⁻¹ which is revealed to couple
with C-C and C-N stretching vibrations. The modes assigned at 1588
and 1423 cm⁻¹ for scissoring and rocking modes in FT-Raman spectrum. The wagging and twisting modes are expected at 1361 cm⁻¹
and 514 cm⁻¹ in FT-IR and FT-Raman spectrum, respectively.
3.4.4. CH₃ vibrations

Methyl group attached along with methylene and oxygen atom to benzene ring. Methyl group vibrations are electron-donating substituent and can vibrate in nine different ways viz., CH₃-symmetric and asymmetric stretching, in-plane and out-of-plane bending modes and CH₃ torsion. Methyl C–H stretching mode appears at lower frequencies than those aromatic ring at 3000-2900 cm⁻¹. The anti-symmetric and symmetric deformations of the methyl group attributed in the region 1465-1440 cm⁻¹ and 1040-990 cm⁻¹ respectively [31, 32]. In the present investigation, the asymmetric stretching mode appear at 3040 cm⁻¹ and 2983 cm⁻¹ in the FT-IR and FT-Raman spectrum, respectively, and symmetric stretching mode appear at 2961 cm⁻¹ in the FT-Raman spectrum. The methyl rocking mode vibration usually appears within the region 1070-1010 cm⁻¹. The CH₃ rocking and torsional vibrations are assigned which listed in Table 2.

3.4.5. C–F vibrations

The C–F stretching modes are difficult to determine which is due to coupling with other bending modes of vibration. The C–F stretching modes are obtained for several fluoro benzenes in the region 1000-1300 cm⁻¹ which are strongly coupled with C–H in-plane bending vibrations [33]. In this compound the two fluorine atoms are attached in the position of ortho and meta places of the parent ring. In 3, 5-difluoroaniline, Pathak et al. [34]. observed the C–F stretching modes that are coupled with C–N and C–C stretching vibrations and C–H in-plane bending vibrations are assigned at 1355 cm⁻¹ (IR) and 1348 cm⁻¹ (R) and 1115 cm⁻¹ (IR) and 1113 cm⁻¹ (R). Accordingly for 4EDFB, the C–F stretching vibration observed at 1080 cm⁻¹ and 1065 cm⁻¹ in Raman spectrum. For the present compound, the heavy substituents are attached to fluorine atoms tend to shift the C–F stretching modes to lower wave numbers. These wave numbers are coinciding well with earlier reports [35, 36]. Generally, the C–F in-plane bending vibration is obtained at 250-350 cm⁻¹.
3.4.6. C–C vibrations

The carbon atom in the benzene ring undergoes coupled vibration due to presence of conjugate substituent which give maximum C-C stretching modes of four bands that appear in the region 1660–1420 cm⁻¹ [37]. In general, Varsanyi assigned that the variable intensity of five bands can be observed at 1625–1590 cm⁻¹, 1590–1575 cm⁻¹, 1540–1470 cm⁻¹, 1460–1430 cm⁻¹ and 1380–1280 cm⁻¹, in this region [38]. For 4EDFB, the C-C stretching vibration has observed at 1414 cm⁻¹ in FT-IR spectrum. For 6-dichlorobenzamide, Yaping Tao et.al [13]. have obtained at 720 cm⁻¹ [37]. In general, Varsanyi assigned the variable intensity of five bands can be observed at 1625–1590 cm⁻¹, 1590–1575 cm⁻¹, 1540–1470 cm⁻¹, 1460–1430 cm⁻¹ and 1380–1280 cm⁻¹, in this region [38]. For 4EDFB, the bands obtained at 1654 cm⁻¹, 1629 cm⁻¹, 1605 cm⁻¹, 1467 cm⁻¹, 1462 cm⁻¹, 1436 cm⁻¹, 1398 cm⁻¹, 1334 cm⁻¹, and 1294 cm⁻¹ in the FT-IR and FT-Raman spectrum are assigned to the C-C stretching modes. The C-C in-plane and out-of-plane bending vibrations are usually obtained in the range at 1000–675 cm⁻¹ and 450–112 cm⁻¹. In the present compound, the wave numbers of in-plane and out-of-plane bending vibrations are observed which are listed in Table 2.

3.4.7. C–N vibrations

It is very difficult to identify the C–N vibration due to the possible mixing of several bands. The C–N stretching vibrations appear in the region 1200–1400 cm⁻¹. Polat et.al [39], reported the C–N stretching vibrations in the region 1300–1350 cm⁻¹ for the imidazole ring. For 4EDFB, the C–N stretching vibration has observed at 1414 cm⁻¹ in FT-IR spectrum. For 6-dichlorobenzamide, Yaping Tao et.al [13]. have obtained the C–N in-plane and out-of-plane bending vibrations at 571 cm⁻¹ and 74 cm⁻¹. For 4EDFB, the C–N bending vibrations are observed at 720 cm⁻¹ (IR) 718 cm⁻¹ (R) and 44 cm⁻¹ (IR). The experimental values of C–N stretching and bending modes show good agreement with theoretical values.

3.4.8. C=O and C–O vibrations

The Carbonyl stretching C=O vibrations are appear in the region of 1850–1600 cm⁻¹ [16]. The IR bands located at 1734 cm⁻¹ for C=O stretching vibration and the bands obtained at 1129 cm⁻¹ and 1116 cm⁻¹ for C–O stretching vibrations in FT-Raman spectrum. The C=O and C–O in-plane and out-of-plane bending vibrations have been identified and are labeled in Table 2. These values are in good agreement with the theoretical calculations performed at B3LYP with various basis sets.

3.5. Scale factors

The quantum chemical calculation reveals the overestimated calculated vibrational modes when compared to the experimental values due to the anharmonicity that can be corrected by introducing scale factors to minimize overall deviation using MOLVIB 7.0 by sundius [20]. The Root Mean Square (RMS) values of IR and Raman wave numbers were evaluated using the following equation [40, 41].

\[
\text{RMS} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (v_{\text{exp}} - v_{\text{calc}})^2}
\]

The RMS errors are found to be 106.6 cm⁻¹ at B3LYP/6-31+G (d,p) for unscaled frequencies and hence to scale down the calculated vibrational frequency along with the experimental ones, the scale factors are refined that resulted in the RMS deviation of 6.61 cm⁻¹ between the experimental and scaled quantum wave numbers. The selective scale factors for present molecule are predicted to be 0.898 for N–H stretching, 0.956 for C–H stretching and 0.892 for bending vibrations (in-plane and out-of-plane).

3.6. Aromaticity

The analysis of aromatic character is considered as one of the most fundamental concepts in current chemistry by which the special stability of benzene is explained. Elucidation of aromaticity depends on various significant categories and the main criteria of aromaticity are:

(i) Structural – bond length equalization.
(ii) Energetic – increased stability.
(iii) Negative Nucleus Independent Chemical shift (NICS) – remarkable chemical shift.
(iv) Magnetic – high magnetic anisotropies.

Harmonic Oscillator Model of Aromaticity (HOMA) is the most significant indicator to express geometrical aspects of aromaticity of π–electron molecules. Decrease of aromaticity of the molecule can be realized by two different categories namely GEO and EN respectively. Here GEO is defined as an increase of the bond distance alteration and EN is the extension of the mean bond distance. These two characteristics have been discovered due to the applications of the HOMA index as described by Krygowski et. al [42, 43, 44].

The HOMA index is expressed as [45]:

\[
\text{HOMA} = 1 - \left[\frac{\alpha}{n} \sum (R_{opt} - R_{av}) + \frac{\alpha}{n} \sum (R_{av} - R_{i})\right] ^2
\]

(4)

\[
\text{EN} = \alpha (R_{opt} - R_{av})^2
\]

(5)

\[
\text{GEO} = \frac{\alpha}{n} \sum (R_{av} - R_{i})^2
\]

(6)

Here, \(n\) is the total number of bonds, \(R_{i}\) stands for running bond length, \(R_{av}\) stands for the average bond length and \(\alpha\) (for C-C bonds \(\alpha = 257.7\)) is an empirical constant fixed to HOMA = 0 and HOMA = 1 for the system with equal bonds to optimal value \(R_{opt}\) (for C-C bonds \(R_{opt} = 1.388\)) considered for fully aromatic systems. The HOMA index can be smaller than 1 for compounds with \(R_{ave} > R_{opt}\). For instance, the reported value of HOMA index of 3-amino –4-methoxy benzamide is 0.9812 [40]. The calculated entities of the HOMA index for the present molecule have been presented in Table 3. The presented value shows that there was no deviation from aromaticity.

### Table 3

| parameters | \(R_{av}\) | \(R_{opt}\) | \(\alpha\) | GEO | EN | HOMA |
|------------|------------|------------|----------|-----|----|------|
| Values (Å) | 1.398      | 1.388      | 257.7    | 0.0153 | 0.0258 | 0.9589 |

The calculated entities of HOMA index of 4 - Ethoxy-2,3-difluoro benzamide using B3LYP/6-31+G (d,p).
done using B3LYP/6-31 +G (d,p) basis set. The pictorial representation of HOMO-LUMO is labeled in Fig. 6. The HOMO-LUMO plot describes the information about physical properties of molecules and provides insight into the nature of the reactivity. HOMO is localized over entire molecule except hydrogen atoms and LUMO is delocalized on the entire molecule except ethoxy group of the molecule [47]. The color codes of red to green indicate the positive and negative phase of the molecule. The frontier molecular orbital energy gap (E_LUMO - E_HOMO) is significant to imply the molecular stability with respect to further chemical reaction. In this case, the energy gap of HOMO and LUMO is predicted to be 5.38191 eV. The HOMO-LUMO gap of 6-dichlorobenzamide is found to be 5.944 eV [13]. A large value of frontier orbital gap is associated with a low chemical reactivity and eventual charge transfer occurs within the compound [48, 49]. The molecule with large HOMO-LUMO gap means less polarizable and chemically stable compound.

\[
\text{HOMO Energy} = -6.91841 \text{ eV} \\
\text{LUMO Energy} = -1.5365 \text{ eV} \\
\text{Energy gap } \Delta E = 5.38191 \text{ eV}
\]

3.8. Global chemical descriptors

The concept of chemical reactivity of molecule is related to a large part theoretical chemistry which is based on the frontier molecular orbital theory. The density functional theory has extraordinary potential to obtain the global reactivity descriptor which implies the information about the general behavior of the molecules [50]. These are the electronic chemical potential (μ), hardness (η), and softness (s), electro negativity (χ) and electrophilicity (ω). Global hardness measures the resistance of an atom to a charge transfer and softness describes the
ability of an atom to receive electrons.

According to Euler-Lagrange equation in density functional theory, the general definitions [51] of chemical parameters are shown to be

\[
\mu = \left( \frac{\partial E}{\partial N} \right)_{\nu} = \frac{1}{2} (I - A)
\]

(8)

\[
\eta = \left( \frac{\partial \mu}{\partial N} \right)_{\nu} = \frac{\partial \mu}{\partial N}
\]

(9)

Where, E, N and \( \eta \) are energy, number of electrons and external potential of the system, respectively.

The global softness, \( S \) is simply the reciprocal of the global hardness which measures the extent of chemical reactivity.

\[
S = \eta^{-1} = \left( \frac{\partial N}{\partial \mu} \right)_{\nu}
\]

(10)

Most part of theoretical chemistry, is related to reactivity which is based on the concepts of frontier molecular orbital energies such as highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital. According to Koopman’s theorem, ionization potential (I) and the electron affinity (A) are related to the energies of HOMO and LUMO, respectively.

And the above equations can be modified and are defined as

Chemical potential \( \mu = \frac{I - A}{2} \)

(11)

Global hardness \( \eta = \frac{I - A}{2} \)

(12)

Electro negativity \( \chi = \frac{I + A}{2} \)

(13)

The global electrophilicity index \( \omega \) can be described using \( \mu, \eta \) as follows.

\[
\omega = \frac{\mu^2}{2\eta}
\]

(14)

This new reactivity index measures the stabilization in energy. The evaluated chemical descriptors of EHOMO, ELUMO, \( \mu, \lambda, \eta, \chi \), \( S \) and \( \omega \) for 4EDFB are summarized in Table 4. The calculated results show that, the negative chemical potential value is \( \mu = -4.2275 \) eV and indicates more stability of the title molecule. Global hardness measures the reactivity and softness and describes the ability of an atom to receive electrons. A good electrophile described by a large value of electrophilicity while good nucleophile described by a small value of nucleophilicity [52, 53].

### 3.9. Local reactivity descriptors

#### 3.9.1. Fukui function

Apart from the global properties, the two local reactivity parameters such as fukui function and local softness are necessary for difference treating the reactive behavior of atoms in forming molecule. The fukui function or frontier function used to predict the reactivity sites in a molecule and to determine electrophilic and nucleophilic attack, respectively.

| Atom | Neutral (a.u.) | Cation (N-1) (a.u.) | Anion (N+1) (a.u.) | \( \gamma_f \) (a.u.) | \( \gamma_i \) (a.u.) | \( \delta_f \) (a.u.) | \( \delta_i \) (a.u.) | \( \Delta \varepsilon_f \) (a.u.) |
|------|----------------|----------------------|---------------------|-------------------|-------------------|------------------|------------------|------------------|
| C1   | 0.9682         | 0.7248               | 0.6167              | -0.2434           | 0.3514            | 0.0546           | -0.5948          |
| C2   | -0.7525        | -0.3820              | -0.2959             | 0.3706            | -0.4566           | -0.0430          | 0.8272           |
| C3   | 0.9181         | 1.0212               | 0.2881              | 0.1031            | 0.6300            | 0.3655           | -0.5269          |
| C4   | -0.2600        | -0.2489              | -0.6250             | 0.0111            | 0.3650            | 0.1881           | -0.3539          |
| C5   | 0.1000         | 0.1620               | 0.5189              | 0.0019            | -0.4188           | -0.2085          | 0.4207           |
| C6   | -0.5441        | -0.0710              | -0.6849             | -0.1269           | 0.1408            | 0.0070           | -0.2677          |
| C7   | 0.5177         | 0.5306               | 0.5150              | 0.0130            | 0.0027            | 0.0078           | 0.0103           |
| F8   | -0.3619        | -0.3022              | -0.3886             | 0.0597            | 0.0266            | 0.0432           | 0.0331           |
| F9   | -0.3647        | -0.3135              | -0.3785             | 0.0512            | 0.0138            | 0.0325           | 0.0374           |
| O10  | -0.3580        | -0.2134              | -0.3505             | 0.1446            | -0.0075           | 0.0685           | 0.1521           |
| H11  | 0.1456         | 0.1971               | 0.0947              | 0.0514            | 0.0509            | 0.0512           | 0.0005           |
| H12  | 0.1770         | 0.2100               | 0.1358              | 0.0329            | 0.0412            | 0.0371           | -0.0083          |
| O13  | -0.5391        | -0.3657              | -0.6404             | 0.1734            | 0.1013            | 0.1374           | 0.0722           |
| N14  | -0.5951        | -0.4803              | -0.5897             | 0.1148            | -0.0054           | 0.0547           | 0.1201           |
| H15  | 0.3325         | 0.3585               | 0.2774              | 0.0260            | 0.0551            | 0.0406           | -0.0291          |
| H16  | 0.3175         | 0.3283               | 0.2673              | 0.0108            | 0.0303            | 0.0205           | -0.0195          |
| C17  | -0.0600        | -0.0454              | 0.0667              | 0.0146            | -0.1207           | -0.0560          | 0.1413           |
| H18  | 0.1603         | 0.1835               | 0.1371              | 0.0233            | 0.0232            | 0.0232           | 0.0001           |
| H19  | 0.1483         | 0.1953               | 0.1067              | 0.0470            | 0.0415            | 0.0443           | 0.0055           |
| C20  | -0.4245        | -0.3835              | -0.5248             | 0.0410            | 0.1003            | 0.0707           | -0.0593          |
| H21  | 0.1615         | 0.1872               | 0.1431              | 0.0257            | 0.0184            | 0.0221           | 0.0074           |
| H22  | 0.1543         | 0.1960               | 0.1197              | 0.0417            | 0.0346            | 0.0382           | 0.0070           |
| H23  | 0.1590         | 0.1714               | 0.1712              | 0.0124            | -0.0122           | 0.0001           | 0.0245           |
The condensed form of the Fukui function for an atom \( k \) in a molecule can be defined as \([54, 55]\).

\[
\begin{align*}
  f_{k+} &= q_k^{(N+1)} - q_k^{(N)} \quad \text{for molecule } k \text{ as an electrophile} \\
  f_{k-} &= q_k^{(N)} - q_k^{(N+1)} \quad \text{for molecule } k \text{ as a nucleophile} \\
  f_{k0} &= q_k^{(N+1)} - q_k^{(N+1)} \quad \text{for molecule } k \text{ as a radical}
\end{align*}
\]

Where the parameters \( q_k^{(N)}, q_k^{(N+1)} \) and \( q_k^{(N+1)} \) are the charges of molecule \( k \). \( N, (N-1) \) and \( (N+1) \) electrons for neutral, anion and cation, respectively at the optimized geometry of the molecule with \( N \) electrons. In order to determine the pinpoint distribution of the atomic sites on the molecule, the Fukui function was characterized through above three equations which evaluate the reactivity at atomic resolution. In this case, Mulliken population analysis was used to calculate the Fukui function of the title molecule at B3LYP/6-31+G (d, p) basis set. The evaluated reactivity parameters results exhibit that the more reactive sites for electrophile is \( C_3 = 0.6300 \), nucleophile is \( C_3 = 0.33706 \) and radical is \( C_2 = 0.827198 \) a. u \([56, 57]\) which are reported in Table 5 and the graphical representation is shown in Fig. 7.

### Local softness

Local softness is extensively successful tool in determining the site selectivity and regio chemistry. A mutually related reactivity parameters of Fukui function \( f(r) \) and local softness \( s(r) \) can be written as

\[
s(r) = \frac{s}{f(r)}
\]

The local softness describes the reaction path and discovers the type of reactivity.
of chemical bond occurs between molecules [58, 59]. The concept of generalized philicity was introduced by Chattaraj et al. [60]. It contains the different global reactivity and local selectivity descriptors and also provides the information regarding electrophilic and nucleophilic power of a given atomic site in a molecule. Recently, the electrophilicity was used to elucidate the toxicity of benzidine and polycyclic aromatic hydrocarbons (PAHs) [61]. In order to obtain the second order non linearities (hyperpolarizabilities), conjugated organic molecules are substituted with electron-donor and electron-acceptor end groups. Generally β depends on the strength of the donor and acceptor groups with strong electronic coupling through the conjugated π-bridge [67].

The static response properties of a molecule can be expressed by expanding the field-dependent energy $E$ (F) which is expressed by [68].

$$E(F) = E_0 - \sum F_i \alpha_{ik} F_i F_j - \frac{1}{2} \sum \beta_{ijk} F_i F_j F_k - \frac{1}{24} \sum \gamma_{ijkl} F_i F_j F_k F_l$$

(21)

where $E$ is the energy of a molecule under the electric field $F$, $E_0$ is the unperturbed energy of a free molecule, $F_i$ is the vector component of the electric field in the $i$ direction and $\mu$, $\alpha$, $\beta$, $\gamma$ are the dipole moment, linear polarizability, first and second order hyper polarizabilities respectively.

The complete equations for calculating the magnitude of dipole moment ($\mu$), polarizability($\alpha$), anisotropy of the polarizability ($\Delta \alpha$), first hyperpolarizability ($\beta$) and second hyperpolarizabilities ($\gamma$) using the $x,y,z$ component are explained as follows [69].

$$\Delta \alpha = \frac{1}{\sqrt{3}} (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6 (\alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2)$$

(24)
Anisotropic polarizability

First hyperpolarizability $\beta_1 = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$

Here

$\beta_s = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$

Second order hyperpolarizability $\gamma = \gamma_{xxx} + \gamma_{xyy} + \gamma_{xzz} + \frac{2}{5}(\gamma_{xyy} + \gamma_{xzz} + \gamma_{yzz})$

In this study, dipole moment, polarizabilities, and the second and third order polarizabilities or hyperpolarizabilities of the title molecule were investigated by using B3LYP at 6-31+G (d,p) basis set. The calculated values of $\mu, \alpha, \Delta\alpha$, $\beta$ and $\gamma$ are tabulated in Table 7. The dipole moment resonates molecular charge distribution and it can be describes the charge movement across molecule. The total dipole moment was found to be 3.5277 Debye. In NLO system, the magnitude of the first hyperpolarizability is the most significant factor. The negative value of $\beta$ indicates that the charge flows in the opposite direction to the dipole moment in the excitation. The domination of hyperpolarizability value in the particular component $\beta_{yzz} = 14.68088$ implies a substantial delocalization of charges in this direction. The average polarizability ($\alpha$) and first hyperpolarizability ($\beta$) are $14.16\times10^{-24}$ esu and $6.7645\times10^{-30}$esu respectively, which are greater than carbomide. The carbomide is the most archetypical compound for second harmonic generation (SHG) with in the NLO system [70, 71].

3.11. Molecular electrostatic potential (MEP)

It should be noted that any chemical system creates an electrostatic potential around itself. Molecular electrostatic potential (MEP) is very important tool to investigate and correlate between the molecular structure and the physiochemical property relationship of the molecules with including biomolecules and drugs [72]. The electrostatic potential surface was mapped over the electron density which displays the molecular size, shape and charge distribution. It gives information about the molecules interaction with one another and simultaneously ESP has been used extensively for predicting reactive behavior and inter and intra-molecular interaction of chemical systems as well as hydrogen bonding [73]. The significance of MEP provides a visual method to understand the relative polarity of the molecule and simultaneously the different values of the electrostatic potential represented by different colours; blue, red and green represented region of most positive, most negative and zero electrostatic potential, respectively. It means, potential increases in the order blue > green > yellow > orange > red. The negative region (red, orange and yellow) indicates electrophilic reactivity and the positive region to nucleophilic reactivity. Red indicates the strongest repulsion, blue indicates the strongest attraction and green indicates neutral electrostatic potential region. In order to predict reactive sites of electrophilic and nucleophilic attack and for the title molecule, the 3D molecular electrostatic (MEPS) potential and total electron density are illustrated in Fig. 8. In this compound the MEP shows that the negative potential sites on electronegative atoms and the positive potential sites on hydrogen atoms [74].
3.12. Hydrogen bonding

A dimer is an oligomer composed of two structurally similar monomers joined by chemical bonds that can be either covalent or intermolecular. Non covalent dimers namely carboxylic acids, acetic acids and protein dimer can be formed by hydrogen bonding. Hydrogen bonds are very abundant in nature and they are inherently present in number of organic and bio-molecules. Hydrogen bond is an important non-covalent interaction in chemistry and biology and which can be divided into two categories namely intramolecular and intermolecular hydrogen bonds based on donar and accepters reside in different manner. In intramolecule hydrogen bonds, the donar and accepter atoms exist in the same molecule and in intermolecular hydrogen bonds, donar and acceptor groups are reside in different molecules [75]. The various strategies are employed to elucidate the in-depth understanding of inter and intra molecular hydrogen bonds. For example, P. Dhanishta et.al studied the existence of intra molecular hydrogen bonds in synthesized benzoyl phenyl oxalamide derivatives using NMR studies and DFT computations [76, 77].

Intermolecular interactions play a pivotal role in biomolecules and drug designs and to interpret the molecular structure and deformability. Particularly, hydrogen bond is evolved in three dimensional conformations of proteins and peptide catalysis [78]. A special type of electrostatic dipole-dipole attraction occurs when hydrogen atom strongly bonded to electronegative atom exists in the vicinity of another electronegative atom such as nitrogen, oxygen or fluorine bearing a lone pair of electrons. Due to this significance, for the present compound the hydrogen bond analysis has been carried out using dimer structure is depicted in Fig. 9 and the corresponding values are illustrated in Table 8. A remarkable reduction is observed in the intermolecular hydrogen bond lengths (14N–15H = 1.736 Å and 13O–38H = 1.74 Å) when compared the sum of van der walls radii (O–H = 2.70 Å and N–H = 2.74 Å) which strongly confirms the presence of intermolecular hydrogen bonds [79, 80, 81].

3.13. Mulliken analysis

The Calculation of Mulliken atomic charges have an important role in the application of quantum mechanical calculations to atomic charges which causes dipole moment, molecular polarizability and electronic properties of molecular systems [82]. The positive and negative charge distribution is significant role to increasing or decreasing the bond length between the atoms of the molecule. In order to determine the electron population of each atom calculated by Mulliken charges of 4EDFB using B3LYP/6–31 + G (d,p) basis set and the corresponding values are illustrated in Table 9. The results show that, all hydrogen atoms exhibits positive which are an acceptor and the values varies from 0.1483 to 0.3325. The hydrogen atoms where located at the different functional

### Table 8

| Bond Length (Å) | B3LYP/6-31+G (d,p) Method |
|-----------------|----------------------------|
| O13 – H38 - N37 | 1.736                      |
| N37 – H38       | 1.042                      |
| N14 – H15 – O36 | 1.736                      |
| O36 – H15       | 1.042                      |

### Table 9

| Atoms | Mulliken Charges (a.u) |
|-------|------------------------|
| 1C    | 0.968151               |
| 2C    | -0.752525              |
| 3C    | 0.918079               |
| 4C    | -0.259989              |
| 5C    | 0.100941               |
| 6C    | -0.544098              |
| 7C    | 0.517658               |
| 8F    | -0.361913              |
| 9F    | -0.364727              |
| 10O   | -0.358014              |
| 11H   | 0.145645               |
| 12H   | 0.177034               |
| 13O   | -0.539418              |
| 14N   | -0.595057              |
| 15H   | 0.332462               |
| 16H   | 0.317547               |
| 17C   | -0.05999               |
| 18H   | 0.160252               |
| 19H   | 0.14825                |
| 20C   | -0.4245                |
| 21H   | 0.161473               |
| 22H   | 0.154336               |
| 23H   | 0.159033               |

Fig. 9. Dimer structure of 4-ethoxy -2, 3-difluoro benzamide.
group such as methylene (H18 = H19), methyl (H21 = H22 = H23) and amide groups (H15 = H16). The highly positive hydrogen atoms H15 and H16 is due to fact that accepting the electrons from negatively charged nitrogen atom N14. Within the benzene ring, three carbon atoms C2, C4 and C6 are negative which are donar atoms while rest of three atoms are positive. The highly negative carbon atom C2 is due to substitution of the highest electronegative atom F8 which makes the neighboring atoms C1 and C3 as positive [83]. The graphical representations of charges are shown in Fig. 10.

4. Conclusion

In the present investigation, the experimental and theoretical vibrational analysis of 4-ethoxy-2,3-difluoro benzamide (4EDB) have been carried out based on scaled quantum mechanical force field approach using Density functional theory. The differences between the scaled and observed values of the fundamentals are very small which are coinciding with experimental results. The vibrational spectral investigation reveals the presence of intramolecular charge transfer from electron donar to acceptor, which leads to NLO activity of the compound. The NLO activity of the present compound was also confirmed by the predicted large value of first order hyperpolarizability. HOMO-LUMO energy gap enhance the stability of the molecule. The chemical descriptors elucidate the reactivity and site selectivity of the molecule. The different substitution reaction mechanisms of the molecule have been discussed by using Fukui function and local softness. A special type of dipole-dipole interaction was performed using dimer structure. The MEP explicate that the positive and negative potential sites are on around the hydrogen atom and amide group. The net charge distribution of the title molecule was computed by the Mulliken population analysis.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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