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## Synthesis, Characterization, Crystal structure and DFT calculations of 1-benzofuran-2-carboxylic acid

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### ABSTRACT

*In this study, 1-benzofuran-2-carboxylic acid was synthesized and characterized by FT-IR, <sup>1</sup>HNMR and single crystal XRD analysis. The compound crystallizes in monoclinic system with space group P2<sub>1</sub>/n and Z = 4. Its vibrational frequencies and optimized geometric parameters has been calculated using DFT method with UB3LYP/6-31G (d, p) basis sets by Gaussian 03 software. The calculated vibrational frequencies and optimized geometric parameters (bond lengths and bond angles) were compared with experimentally measured values and found to be in good agreement with each other. Additionally, molecular electrostatic potential maps, density of states, frontier molecular orbitals and the other related molecular energy values have been evaluated using the same theoretical calculations.*

**Keywords:** 1-benzofuran-2-carboxylic acid, DOS, FT-IR spectrum, Density functional theory, X-ray diffraction.

### INTRODUCTION

Benzofurans are important heterocyclic compounds, which are naturally occurring and exhibit not only remarkable biological activities but also acts as useful building blocks in the synthesis of natural products [1, 2]. Many of the natural benzofurans have physiological, pharmacological and toxic properties [3]. These derivatives have displayed wide range of biological activities such as antibacterial [4], analgesic, anti-inflammatory [5,6], anticancer [7] and cardiovascular [8]. In addition, benzofurans are used in cosmetic formulations [9] and optical brighteners [10, 11]. To the best of our knowledge and literature survey reports reveal that results based on the X-ray study, IR and HOMO-LUMO analysis of the title compound have not been reported. Hence, the present study was taken up to synthesize 1-benzofuran-2-carboxylic acid and establish the chemical structure by IR, <sup>1</sup>HNMR and single crystal x-ray diffraction. The vibrational frequencies and optimized geometric parameters were calculated using the DFT method with 6-31G (d, p) basis sets level.

### MATERIALS AND METHODS

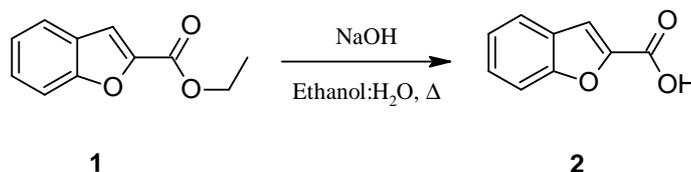
#### *Chemistry*

The purity and progress of reaction was assessed by thin layer chromatography on precoated silica gel plates. Infrared spectrum was obtained with a JASCO FTIR-4100 spectrometer using KBr pellets in the range of 4000 –

400  $\text{cm}^{-1}$  and results was expressed in wave numbers ( $\text{cm}^{-1}$ ).  $^1\text{H}$ NMR spectrum was recorded on a JEOL-400 MHz NMR instrument using  $\text{DMSO-}d_6$  as solvent with chemical shifts being reported as  $\delta$  units relative to TMS.

#### Synthesis of 1-benzofuran-2-carboxylic acid (2)

Ethyl-1-benzofuran-2-carboxylate (**1**) (0.20 g, 0.0010 mmol) was taken in a round bottom flask containing ethanol: water (4:1, 5 mL), to this sodium hydroxide (0.21 g, 0.0052 mmol) was added and refluxed for 4-5 hrs as shown in **Scheme-1**. The reaction was monitored by thin layer chromatography. After completion of the reaction, the reaction mixture was poured into ice cold water and extracted to ethyl acetate layer. Then the organic layer was washed with water and dried over anhydrous sodium sulphate. The organic layer was evaporated under vacuum to get pale yellow crystalline compound (**2**). IR (KBr,  $\text{cm}^{-1}$ ): 3445 (OH str), 3062-2922 (CH str), 1684 (C=O str), 1087-1102 (C-O-C);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  13.5 (s, 1H, OH), 7.80-7.78 (d, 1H, Ar-H,  $J = 8.0$  Hz), 7.71-7.67 (t, 2H, Ar-H,  $J = 8.0$  Hz), 7.52-7.48 (t, 1H, Ar-H,  $J = 16$  Hz), 7.37-7.34 (t, 1H, Ar-H,  $J = 12$  Hz).



**Scheme-1: Synthesis of 1-benzofuran-2-carboxylic acid**

#### X-ray Crystallography

The crystals suitable for X-ray diffraction were developed by slow evaporation of ethyl acetate at room temperature. 1-Benzofuran-2-carboxylic acid was subjected to single crystal X-ray diffraction at 298 K on an Oxford Diffraction X caliber Gemini single crystal X-ray diffractometer using graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The CrysAlisPro software [12] was used for data collection, reduction and absorption correction. The structure of the compound was solved by direct methods and refined on  $F^2$  by full-matrix least-squares procedures using SHELX-97 [13] within the WinG-X suite [14]. The parameter for data collection and structure refinement of the title compound are listed in table 1. All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms bonded to carbon were included in the structure factor in calculated positions using a riding model. The MERCURY [15] packages were used for molecular and packing diagrams.

#### Computational details

For computation, the initial atomic coordinates of the compound were obtained from the experimental structure. The vibrational frequencies were calculated at the same level of theory for the optimized structure using DFT/B3LYP and DFT/HF methods with 6-31G (d, p) basis sets with Gaussian 03 [16] package and Gauss view molecular visualization programs on the personal computer. To investigate the reactive regions of the compound, the molecular electrostatic potential maps were calculated using the same method. Density of States calculations were performed by using Gauss Sum 3.0 [17] package.

## RESULTS AND DISCUSSION

#### Structure description

From single crystal XRD studies, it has been found that the title compound belongs to monoclinic crystal system and possess  $P2_1/n$  space group with cell dimensions  $a = 4.7512(6)$  Å,  $b = 22.133(2)$  Å,  $c = 7.1740(8)$  Å,  $\beta = 96.337(7)^\circ$  and  $V = 749.79(15)$  Å<sup>3</sup>. The molecular structure of the compound with displacement ellipsoids drawn at 50% probability is shown in figure 1a. The molecule is planar as shown in figure 1b and the benzofuran oxygen is anti to the carboxylic -OH group across the C-C bond with root mean squared deviation (r.m.s.d) being 0.013 Å and the O18-C7-C14-O15 torsion being 179.49°. The O15-H15...O16 strong hydrogen bonds forming  $R_2^2(8)$  rings are shown in table 2 and figure 2a. The  $\pi \dots \pi$  interactions along 'a' axis (centroid-centroid distance being 3.7160 Å) helps in forming a one dimensional zig-zag architecture as displayed in figure 2b.

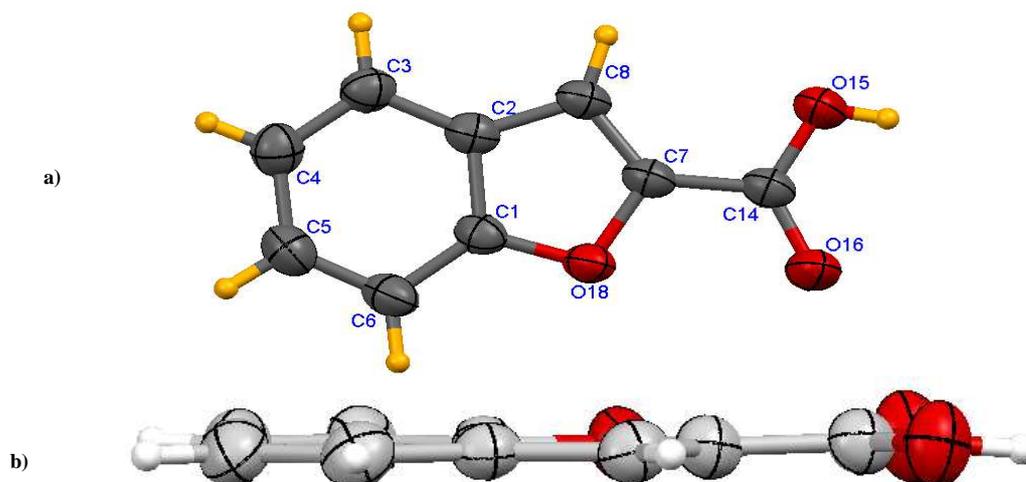


Figure 1: a) ORTEP view of the title compound with atom labeling in color. Atoms are shown as 50% thermal ellipsoids. b) View of the molecule displaying its planarity

### Optimized geometry

The calculated geometric parameters by DFT method and experimental structure parameters (bond lengths and bond angles) were listed in table 3 and figure 3 shows the optimized geometry of the title compound. In carboxylic acid group, the C14-O15, C14-O16 and C14-C7 bond lengths were observed as 1.252(19), 1.278(18) and 1.457(2) Å respectively. These bond lengths have calculated as 1.215 (B3LYP)/1.217(HF), 1.351 (B3LYP)/1.351 (HF) and 1.466 (B3LYP)/1.476 (HF) respectively. In furan ring, the C7-O18, C1-O18 and C7-C8 were calculated as 1.377 (B3LYP)/1.371(HF), 1.364 (B3LYP)/1.368 (HF) and 1.364 (B3LYP)/1.379 (HF) respectively. These bond lengths were observed as 1.387, 1.373 and 1.337 Å respectively. We can see that the C1-C2, C2-C3, C3-C4, C5-C6 and C6-C1 bond lengths in the benzene ring have been calculated from 1.410 to 1.391 Å at B3LYP and from 1.387 to 1.401 Å at HF levels. These bond length ranges from 1.387 to 1.388 Å in X-ray study. The bond angles have been calculated for C1-O18-C7, O18-C7-C14, O15-C14-O16 and O15-C14-O16 as 105.9 (B3LYP)/105.5 (HF), 119.4 (B3LYP)/119.1 (HF), 123.5(B3LYP)/124.5 (HF) and 125.8(B3LYP)/125.5 (HF)<sup>o</sup> respectively and observed as 104.8, 116.8, 124.4 and 124.4<sup>o</sup> respectively.

Table 1: Crystallographic data and structure refinement of title compound

CCDC reference no	CCDC 1032498
Empirical formula	C <sub>9</sub> H <sub>6</sub> O <sub>3</sub>
Formula weight	162.14
Wavelength(Å)	0.71073
Crystal system	Monoclinic
a (Å)	4.7512(6)
b (Å)	22.133(2)
c (Å)	7.1740(8)
α (°)	90
β (°)	96.337(7)
γ (°)	90
V (Å <sup>3</sup> )	749.79(15)
Space group	P2 <sub>1</sub> /n
Z	4
T (K)	293(2)
Crystal size (mm)	0.36 x 0.20 x 0.16
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.436
μ (mm <sup>-1</sup> )	0.109
θ range (°)	1.84 – 30.53
h / k / l indices	-6 / 6, -30 / 31, -9 / 10
Reflections collected	13374
Unique reflection, R <sub>int</sub>	2271 [R(int) = 0.0479]
Goof	1.028
R1 [I > 2σ(I)]	0.0492
wR2 [all data]	0.1430
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.25 and -0.20

**Table 2: Hydrogen bonding parameters for the title compound**

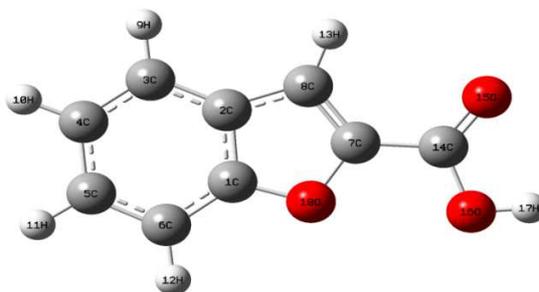
D-H...A (Å)	D-H (°)	H...A (°)	D...A (°)	D-H...A (Å)
O15-H15...O16	0.82 (2)	1.82 (2)	2.6239 (2)	166 (2)
Cg1...Cg2*	-	-	3.7160	-

Symmetry codes: (i) 2-x, -y, -z; (ii) 1+x, y, z

\*Cg1 and Cg2 are the centroids of the benzene and the furan ring respectively.

**Table 3: Optimized and experimental geometries of the title compound.**

	Expt. Values	B3LYP/ 6-31G(d,p)	HF/ CC-PVDZ
<b>Bond length (Å°)</b>			
C14-O15	1.2522(19)	1.21565	1.21706
C14-O16	1.2784(18)	1.35154	1.35166
C14-C7	1.457(2)	1.46661	1.47687
C7-O18	1.3870(17)	1.37730	1.37114
C1-O18	1.373(2)	1.36446	1.36851
C7-C8	1.337(2)	1.36402	1.37925
C2-C8	1.430(2)	1.43479	1.43833
C1-C2	1.387(2)	1.41086	1.41895
C2-C3	1.397(2)	1.40582	1.41553
C3-C4	1.380(3)	1.38865	1.39791
C4-C5	1.388(3)	1.41037	1.42022
C5-C6	1.372(3)	1.39213	1.40047
C6-C1	1.388(2)	1.39122	1.40116
<b>Bond angle (°)</b>			
C1-O18-C7	104.89(12)	105.90906	105.56370
O18-C7-C14	116.87(13)	119.42958	119.16683
O15-C14-O16	124.46(15)	123.58589	124.55885
C14-C7-C8	131.25(14)	128.58804	128.15692
O18-C1-C2	110.94(13)	110.60204	110.95958
C1-C2-C3	119.01(15)	118.97543	119.02904
C1-O18-C7	104.89(12)	105.90906	105.56370
O16-C7-C14	120.56(13)	121.57711	121.39791
O15-C14-O16	124.46(15)	125.84218	125.46657
O18-C1-C6	125.48(14)	119.42958	119.16683
C4-C5-C6	122.36(17)	123.58589	124.55885

**Figure 2: Optimized geometry of title compound**

### Electrostatic potential

The electrostatic potential is well established as an effective tool for interpreting and predicting molecular reactive behavior toward electrophiles [18-20]. The calculated electrostatic potential and magnetic contour map of title compound is depicted in figure 4a & b respectively. It shows that the negative potential is localized above and below the plane of furan and oxygen molecules. This result indicates the effective  $\pi$  conjugation among these rings. So, the molecular electrostatic potential map of compound confirms the existence of intramolecular interaction observed in the solid state.

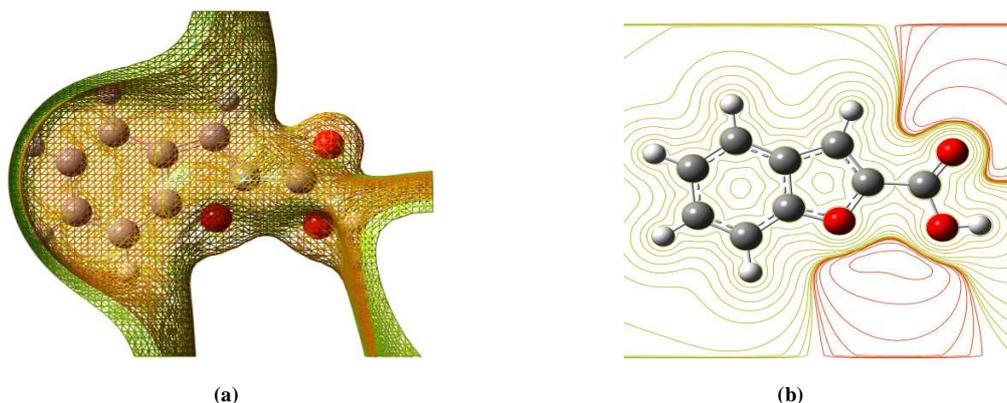


Figure 4: (a) Electrostatic potential map (b) Magnetic contour map of title compound

### HOMO-LUMO Analysis

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are named as frontier molecular orbitals (FMO). The FMO play an important role in optical and electrical properties as well as in quantum and UV-Vis spectra [21-23]. HOMO-LUMO orbitals are the main orbitals involved in the chemical stability of molecule. The HOMO represents donor the ability to donate electrons, while LUMO as an electron acceptor. The distributions and HOMO-LUMO orbitals energy values have been calculated at the UB3LYP/6-31G (d, p) level and are shown in figure 5. The Frontier molecular orbital energy gap relates the stability of compound to hardness. The large HOMO-LUMO gap means hard compound and small energy gap means soft compound, the compound with small energy gap is more polarizable with high chemical reactivity [24]. The energy of separation between the HOMO and LUMO reflects the chemical activity and explains the charge transfer interaction within the molecule, which in turn influences the biological activity. In fact, the compound has the lowest energy gap of 4.735 eV, show the highest activity. The +ve phase represented in red color and -ve phase is represented in green color. By using HOMO and LUMO energy values,  $\eta = (I - A)/2$  (chemical hardness),  $\zeta = 1/\eta$  (chemical softness),  $\mu = 1/2 (E_{LUMO} + E_{HOMO})$  (chemical potential) and the Global electrophilicity index  $\omega = \mu^2/2 \eta$  were also calculated and the results are tabulated in table 4.

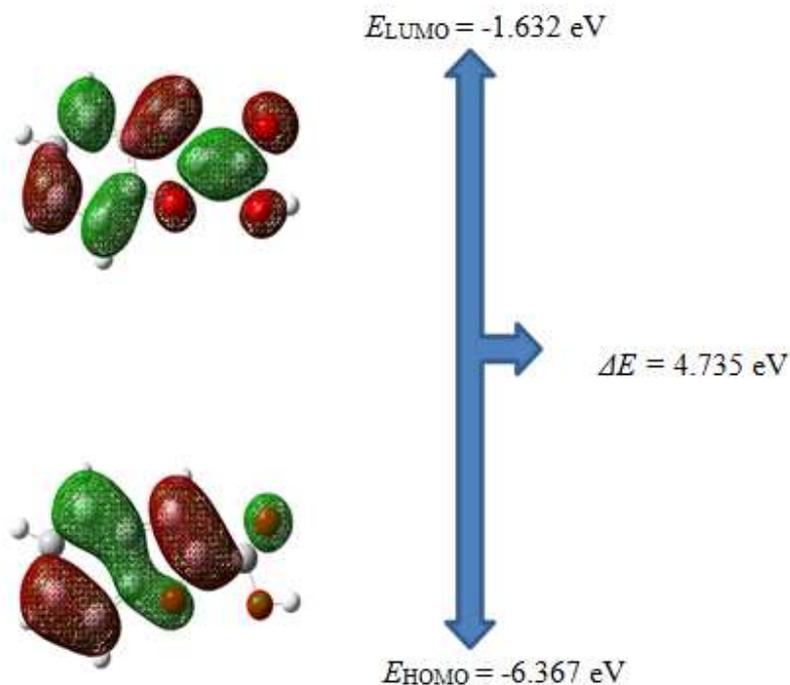


Figure 5: Distribution and energy levels of HOMO and LUMO of title compound

**Table 4: The calculated frontier orbital energies and other molecular properties of compound**

<i>Molecular property</i>	<b>6-31G (d, p)</b>
$E_{\text{HOMO}}$ (eV)	-6.367
$E_{\text{LUMO}}$ (eV)	-1.632
Energy gap (eV)	4.735
Ionization potential ( $I$ )	6.367
Electron affinity ( $A$ )	1.632
Chemical potential ( $\mu$ )	3.999
Global hardness ( $\eta$ )	2.367
Softness ( $\zeta$ )	11.49
Electrophilicity ( $\omega$ )	3.374

**Vibrational Assignment**

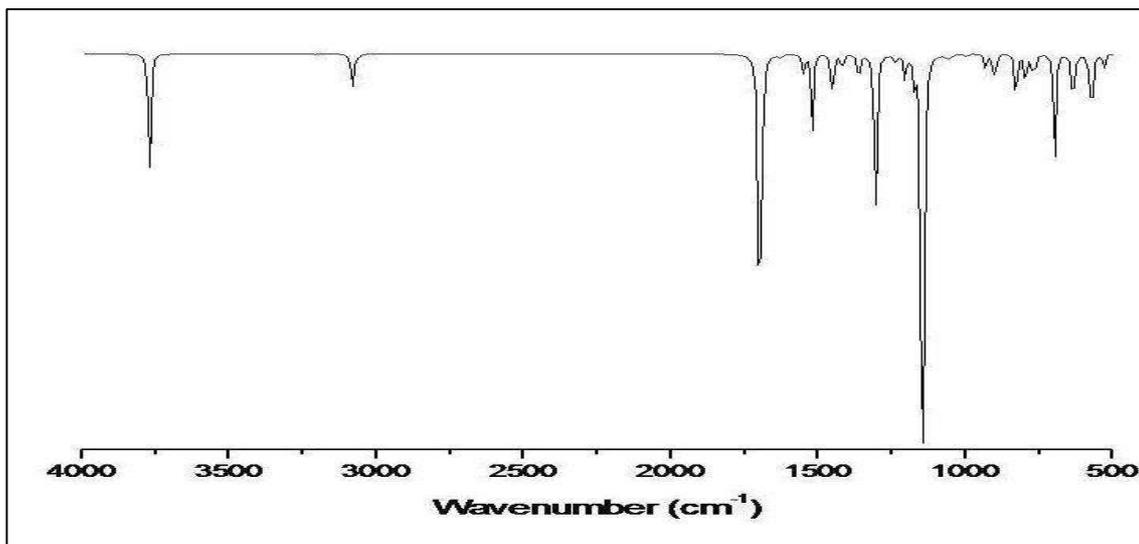
The calculated vibrational frequencies and experimentally measured values are presented in table 5. The calculated FT-IR along with experimental infrared spectra is shown in figure 6a & b respectively.

**C-H vibrations:** The C-H stretching modes were normally observed at 3100-3000  $\text{cm}^{-1}$  [25-27]. In the title compound, these modes were observed at 3062-2844  $\text{cm}^{-1}$  in the FT-IR spectrum and were calculated as 3064  $\text{cm}^{-1}$ . The aromatic C-H in-plane bending vibration bands appear in the region 1300-1000  $\text{cm}^{-1}$ . As seen from the spectrum of the title compound these bands are observed at 1298-1112  $\text{cm}^{-1}$  and calculated as 1305-1136  $\text{cm}^{-1}$ . The C-H out-of-plane bending modes occur in the lower frequency region at 900-675  $\text{cm}^{-1}$  [28-29]. In the title compound, these modes are observed at 884-613  $\text{cm}^{-1}$  and calculated as 904-616  $\text{cm}^{-1}$ .

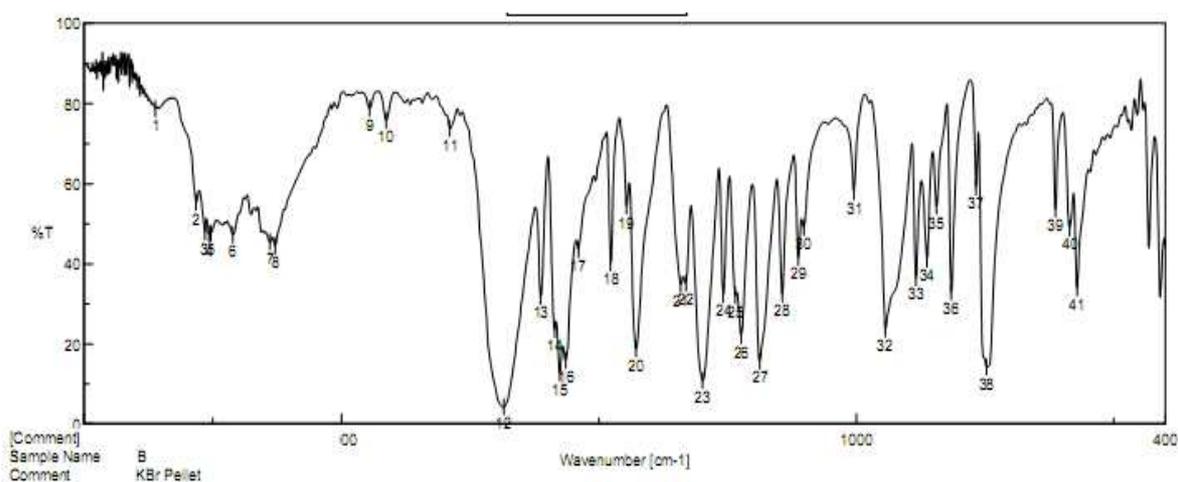
**O-H stretching:** Carboxylic acid dimer display very broad intense O-H stretching in the region 3300-2500  $\text{cm}^{-1}$  and there will be superimposition of weak C-H stretching bands on the broad O-H bands. Hydrogen bonding if present in five or six member ring system would reduce the O-H stretching band to 3200-3550  $\text{cm}^{-1}$  region [30]. In the title compound, the O-H stretching is assigned to 3445  $\text{cm}^{-1}$  in the FT-IR spectrum and calculated as 3768  $\text{cm}^{-1}$ . The O-H in-plane bending vibration appears in the range of 1440-1395  $\text{cm}^{-1}$ . Krishna kumar and Mathammal [31] observed the in-plane bending vibration at 1463  $\text{cm}^{-1}$  in the FT-IR. These in-plane bending is observed at 1477  $\text{cm}^{-1}$ , calculated as 1454  $\text{cm}^{-1}$  in the title compound. One of the characteristic band appear in the dimeric carboxylic acid spectra is out-of-plane bending of the bonded O-H at 920  $\text{cm}^{-1}$ , these band appear in the spectra of the title compound at 944  $\text{cm}^{-1}$  and calculated as 930  $\text{cm}^{-1}$ .

**C=O vibrations:** The C=O stretching bands are more intense and carboxylic acid dimer has a center of symmetry hence only asymmetric C=O stretching absorbs the IR in the region of 1720-1706  $\text{cm}^{-1}$  and internal hydrogen bonding reduces frequency of carbonyl stretching absorption to a greater extent<sup>30</sup>. Hence, in the title compound the C=O stretching is observed at 1684  $\text{cm}^{-1}$  and calculated as 1696  $\text{cm}^{-1}$ .

**Ring vibrations:** There is great mixing of the ring vibrational and substituent modes. Especially, in-plane and out-of-plane modes are the most difficult to assign due to mixing of ring and also substituent modes. Skeletal vibrations, involving C=C stretching vibration absorb in the 1600-1585 and 1500-1400  $\text{cm}^{-1}$  regions [32]. In the present case, these bands are observed at 1613, 1586, 1577 and 1477  $\text{cm}^{-1}$ , were calculated as 1616, 1592, 1584 and 1454  $\text{cm}^{-1}$  respectively. The ring carbon-carbon stretching vibrations appear in the region 1400-1650  $\text{cm}^{-1}$  in benzene derivatives [30]. In general, the bands of variable intensity are observed at 1625-1590, 1590-1575, 1540-1470, 1465-1430 and 1380-1280  $\text{cm}^{-1}$  from the wavenumber ranges by Varsanyi [33-34].



(a)



(b)

Figure 6: (a) Calculated and (b) experimental FT-IR spectra of title compound

Table 5: Vibration wavenumbers obtained for the title compound using UB3LYP/6-31G (d, p)

Modes No	Experimental	Calculated	Vibrational assignments
v <sub>1</sub>	3445	3768	vOH
v <sub>2</sub>	3062	3064	vCH
v <sub>3</sub>	3030	-	vCH
v <sub>4</sub>	3013	-	vCH
v <sub>5</sub>	2844	-	vCH
v <sub>6</sub>	1684	1696	vCO
v <sub>7</sub>	1613	1616	vCC ring + vCO
v <sub>8</sub>	1586	1592	vCC ring
v <sub>9</sub>	1576	1584	vCC ring
v <sub>10</sub>	1477	1454	vCC + δCOH + vCO
v <sub>11</sub>	1446		
v <sub>12</sub>	1341	1367	vCOH + vCC + vCO + δCCO
v <sub>13</sub>	1331	1311	vCC ring
v <sub>14</sub>	1298	1305	vCO + vCC
v <sub>15</sub>	1258	1248	vCC ring + vCO +
v <sub>16</sub>	1223	1205	δCCH + vCC + δCOH
v <sub>17</sub>	1187	1186	δCOH + δCCH + δCO
v <sub>18</sub>	1143	1160	δCOH + δCCH + vCO
v <sub>19</sub>	1112	1136	δCCH + δCCC
v <sub>20</sub>	1087	1060	vCC + δCCH
v <sub>21</sub>	1102	1011	vCC + δCCH + vCO + δCCC
v <sub>22</sub>	944	930	γCH
v <sub>23</sub>	884	904	vCC + vC-COOH
v <sub>24</sub>	863	840	
v <sub>25</sub>	844	832	γCH
v <sub>26</sub>	815	800	
v <sub>27</sub>	767	768	δCCC + vCO
v <sub>28</sub>	747	760	rCCO + γOH
v <sub>29</sub>	613	616	δOCC + δOCO + δCCC
v <sub>30</sub>	586	584	γOH + γCCCO
v <sub>31</sub>	571	576	δCCO + δCCC + δOCO

*v*- Stretching, *δ*- in-plane bending, *γ*- out-of-plane bending.

## CONCLUSION

In the present study, the title compound was synthesized and its structure has been confirmed by IR, <sup>1</sup>HNMR and single X-ray diffraction studies. The single crystal studies shows that the BA crystallizes in monoclinic crystal system with space group P<sub>2</sub><sub>1</sub>/n and are interlinked by O15–H15···O16 strong hydrogen bonds forming a one dimensional zig-zag architecture. The optimized geometric parameters (bond length and bond angles) and vibrational frequencies were compared with experimental data are in good agreement. The Molecular electrostatic potential map shows that –ve potential regions are mainly localized on benzofuran and oxygen atoms. The calculated HOMO-LUMO energy gap corresponds to 4.735 eV and their plot has been presented to understand charge transfer interactions. Additionally, the density of states and the other molecular properties such as Ionization Potential (I), Electron affinity (A), Global Hardness (η), Chemical potential (μ) and Global Electrophilicity (ω) were calculated and tabulated respectively. Since the title compound is an important intermediate in organic synthesis the obtained results will provide helpful information for the further group transformation and derivatization.

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## Supplementary Material

CIF file containing complete crystallographic data for the structure reported in this paper was deposited with Cambridge Crystallographic Data Centre, CCDC No. 1032498 and data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/datarequest/cif](http://www.ccdc.cam.ac.uk/datarequest/cif).

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