

**Spectroscopic and topological investigation of (E)-1-(benzo[d][1,3]dioxol-5-yl)-3-(3-nitrophenyl)prop-2-en-1-one and (E)-1-(benzo[d][1,3]dioxol-5-yl)-3-(4-methoxyphenyl)prop-2-en-1-one**

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**ABSTRACT**

The vibrational patterns of (E)-1-(benzo[d][1,3]dioxol-5-yl)-3-(3-nitrophenyl)prop-2-en-1-one (BDNP) and (E)-1-(benzo[d][1,3]dioxol-5-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (BDMP) are derived from density functional theory (DFT) calculations and the results are compared with experimental one. The various vibration patterns of the specimen have been investigated by Fourier transform infrared and Fourier transform Raman spectroscopy. UV visible spectrum reveals the excitation energies of the molecule and supported by theoretical investigations. Information about the size, shape, charge density distribution and site of chemical reactivity of the molecule has been obtained by mapping electron density with molecular electrostatic potential (MEP). The other molecular properties like charge transfer are explained using Mulliken population analysis of the specimen is also estimated.

**Keywords:** Chalcone, FT-IR, FT-Raman, UV-vis, Mulliken atomic charge and MEP.

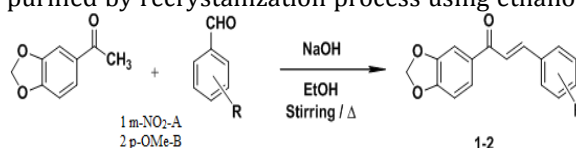
**1. INTRODUCTION**

Chalcones exhibits conjugated double bonds and a completely delocalized  $\pi$ -electron system on two benzene rings. Molecules belonging to such system have relatively less redox potentials and have a significant probability of undergoing electron transfer reactions. The chalcones are an compulsive objective category of compounds which are extensively investigated because of their broad spectrum of biological importance, involve anti-inflammatory<sup>[1]</sup>, anti-invasive, antitumour<sup>[2]</sup> and antibacterial<sup>[3]</sup> properties. They are regarded as promising anticancer agents against most human cancers. Previous literature suggests that chalcones are efficient of inducing apoptosis<sup>[4,5]</sup> and have the capability to uncouple mitochondrial respiration and thus collapse mitochondrial membrane potential<sup>[6]</sup>. Since a number of clinically efficient anticancer drugs have genotoxic impact due to their communication with the amino groups of nucleic acids, chalcones lacking of this important side effects. Because of this vast importance motivated us to synthesise and investigated the properties of chalcones such as BDNP, BDMP. In the present investigation, we are reporting the synthesis, structure, spectroscopic (FT-IR, FR-

Raman, UV-VIS) and topological analysis of BDNP and BDMP.

**2. Experimental****2.1. Synthetic procedure for (E)-1-(benzo[d][1,3]dioxol-5-yl)-3-phenylprop-2-en-1-one derivatives**

Phenylpropenone derivatives were synthesized by mixing stoichiometric amounts of 3,4-methylenedioxy acetophenone (1 mmol) and substituted aromatic aldehyde (1 mmol) in the molar ratio of 1:1 (Scheme 1). The reactants were dissolved in ethanol, thoroughly mixed using a magnetic stirrer for 10 min and 10% NaOH solution was added dropwise at 30 °C. After stirring for 2 h, the contents of the flask were poured into ice-cold water. The solid precipitate formed was collected by filtration, dried and purified by recrystallization process using ethanol



**Scheme - 1: Synthetic scheme of (E)-1-(benzo[d][1,3]dioxol-5-yl)-3-phenylprop-2-en-1-ones.**

as a solvent (yield: 90 %). The completeness of the reaction was monitored by thin layer chromatography.

Optimized molecular structures of BDNP and BDMP are displayed in figure 1.

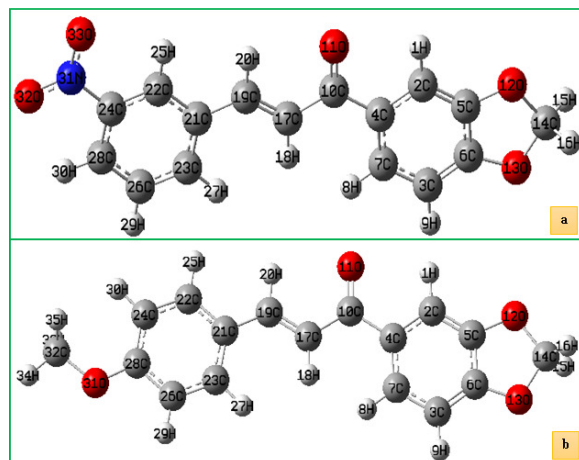


Figure - 1: Optimized molecular structures of BDNP, BDMP.

## 2.2. Experimental details

The FT-IR spectra were recorded using an AVATAR 330 FT-IR by KBr pellet technique in the range of 400–4000  $\text{cm}^{-1}$ . The FT-Raman spectrum was recorded using a BRUKER RFS 100/S Instrument. UV-vis spectrum was recorded using UV-1650PC UV-vis spectrophotometer.

## 2.3. Computational details

Entire calculations have been executed using the Becke three-parameter hybrid functional [7] with well-designed of Lee, Yang, and Parr [8] (B3LYP) in combination with the 6-31G(d,p) basis set as implemented in the GAUSSIAN 09W [9] program package with the default convergence criteria without any constraint on the geometry [10]. The vibrational wave numbers were calculated and the optimized structure of the first chalcone, proving that a true minimum on the potential energy surface was established. NBO calculations were performed using NBO 3.1 program [11] as implemented in the Gaussian 09W. Graphical representations of MESP were calculated from data in structure optimized files, using the Gauss View visualization program [12].

## 3. RESULTS AND DISCUSSION

### 3.1. FT-IR and FT-Raman spectral analyses

Experimental and theoretically predicted FT-IR and FT-Raman spectra of BDNP, BDMP are displayed in figures 2, 3, 4 and 5. The molecular conformation yielded by geometry optimization exhibits no special symmetries and hence the molecule belongs to the  $C_1$  point group. The

deviation from the experiments is less than  $10 \text{ cm}^{-1}$  with few exceptions. Minor variations between the observed and the calculated frequencies could be due to the experimental results belong to solid phase and theoretical calculations belong to a gaseous phase.

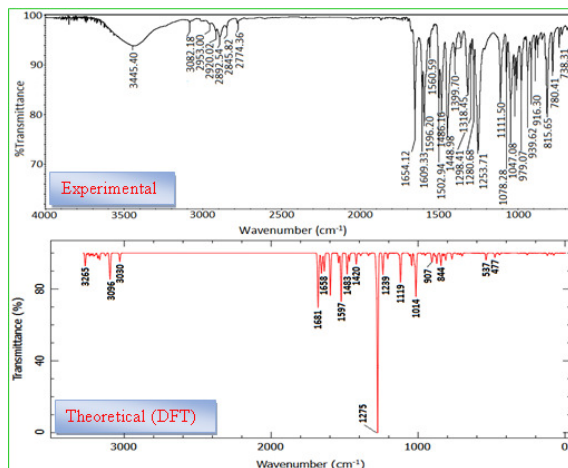


Figure - 2: FT-IR spectrum of BDNP.

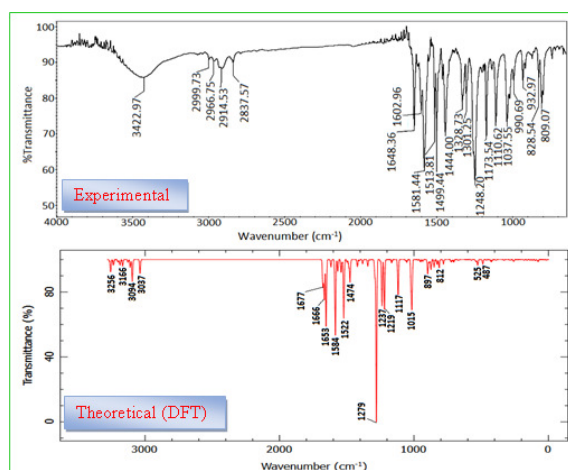


Figure - 3: FT-IR spectrum of BDMP.

### C=O vibrations

The C=O stretching vibration band can be easily recognize from the IR and Raman spectra, because of the degree of conjugation, strength and polarizations. The carbonyl stretching vibrations in ketones are expected in the region  $\sim 1715$  to  $1680 \text{ cm}^{-1}$  [13]. In our case, the C=O stretching bands are observed at  $\sim 1654 \text{ cm}^{-1}$  in FT-IR spectrum and  $\sim 1655 \text{ cm}^{-1}$  in FT-Raman spectrum. Theoretically computed wave numbers are in the range of  $\sim 1749$  and  $1644 \text{ cm}^{-1}$ . This wavenumber shift from expected range is due to the conjugation.

### C-C and C=C vibrations

The six ring carbon atoms undergo coupled vibrations, known as semi circular stretching usually occurring in the region  $1400$  to  $1625 \text{ cm}^{-1}$ . The actual positions of these modes are

determined not so much by the nature of the substituents but by the form of substitution around the ring. The C-C vibrations give rise to characteristic bands in both the observed IR and Raman spectra. The FT-IR bands are observed with variable intensities at ~1448, ~1502 and ~1560 cm<sup>-1</sup>. The FT-Raman observed peaks at ~1562, ~1564 and ~1596 cm<sup>-1</sup>. The theoretically computed wave numbers in B3LYP/6-31G (d, p) method predict at ~1420, ~1483 and ~1597 cm<sup>-1</sup>. Most of the theoretical modes of vibrations are close to the experimental frequencies.

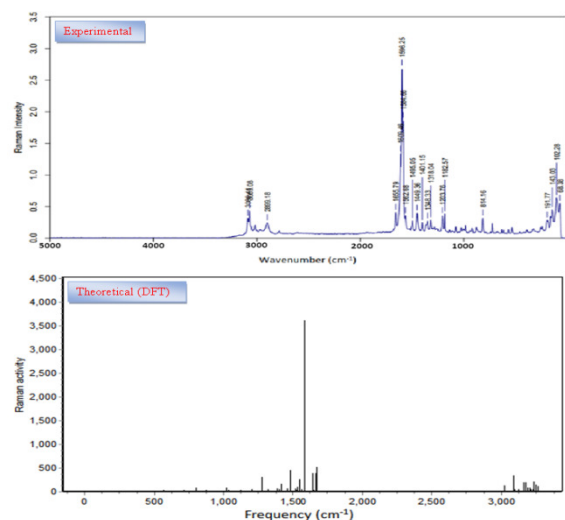


Figure - 4: FT-Raman spectrum of BDNP.

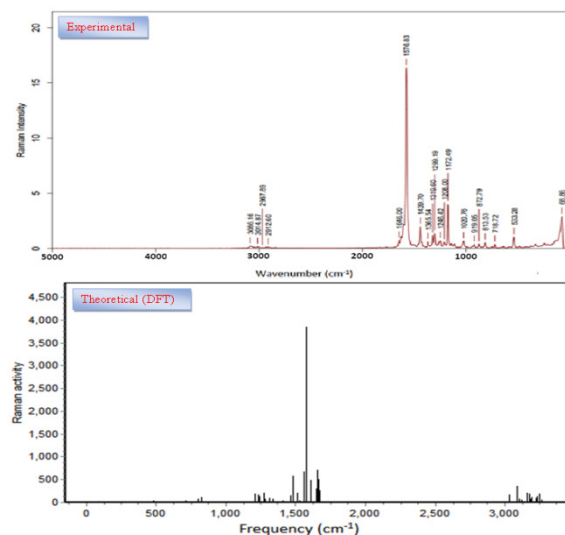


Figure - 5: FT-Raman spectrum of BDMP.

C-H vibrations

The C-H stretching vibration occurs above 3000 cm<sup>-1</sup> and is typically exhibited as a multiplicity of weak to moderate bands<sup>[14]</sup>. The harmonic frequencies are predicted by B3LYP/6-31G (d, p) level at 2884-3201 cm<sup>-1</sup>. The strong bands are observed in FT-IR at ~3445 cm<sup>-1</sup> and strong FT-Raman band at ~3066 cm<sup>-1</sup> are assigned as C-H asymmetric stretching vibration.

The aromatic C-H bending vibration occurs in the region 1400-1000 cm<sup>-1</sup>, the bands are sharp but weak to medium intensity.

3.2. UV-VIS spectral analysis

The optical absorbance spectrum of BDNP, BDMP was recorded in the spectral range of 200 to 500 nm as shown in figure 6. It reveals that the absorbance is minimum in the visible region with UV excitation energy is observed at ~323, ~350 nm. UV-VIS spectral analysis of BDNP, BDMP calculated by TDDFT method and the calculated absorption peak, excitation energy and oscillator strength are ~367, ~385 and 0.833, 0.8485 respectively.

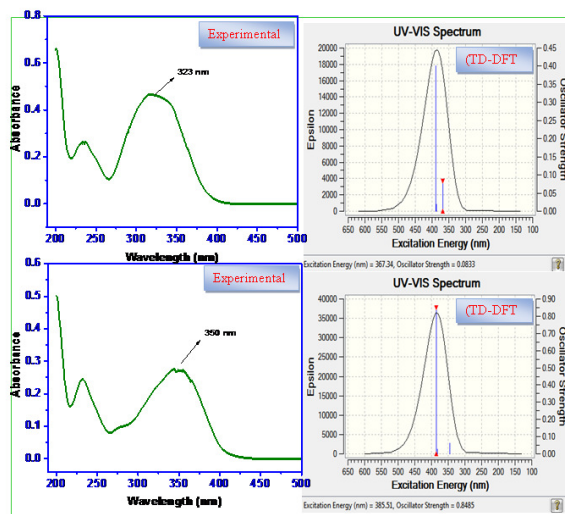


Figure - 6: UV-vis spectrum of BDNP (left) and BDMP (right).

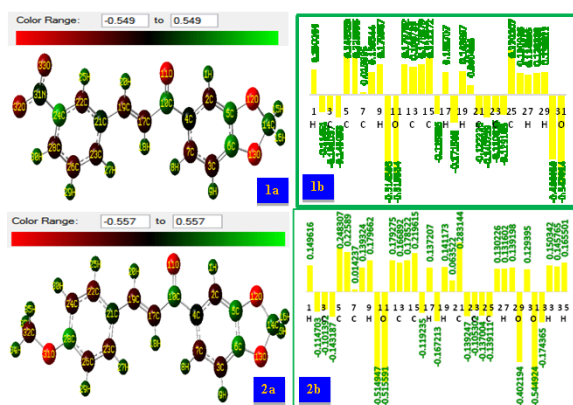


Figure - 7: Mulliken atomic charges of (1)BDNP and (2) BDMP.

3.3. Mulliken population analysis

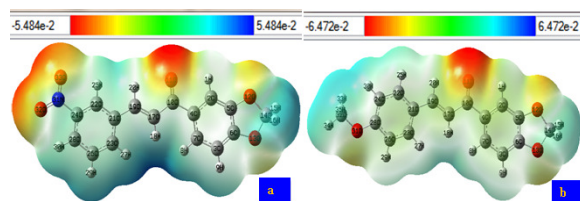
The atomic charge distribution of the various atoms present in the BDNP, BDMP obtained by Mulliken population analysis is shown in figure 7 and the corresponding atomic charge values are made as bar chart displayed in figure 7. Atomic charges have an important role in the application of quantum mechanical calculation to

molecular system. From the listed atomic charge values, the oxygen, Nitrogen atoms had a large negative charge and behaved as electron donors. The C and all the hydrogen atoms exhibit positive charge, which is an acceptor atom of BDNP, BDMP and it could be due to the attachment of more electronegative atoms (O, N).

### 3.4. Topological analysis

#### 3.4.1. Molecular Electrostatic Potential

Electrostatic potential can be studied by means of predictable electronic structure theory package and consequent from experimental X-ray diffraction information and a best technique for investigating the electronic structure of a molecule. The electrostatic interaction are the important phase of the various intra- and intermolecular interactions. The maximum potential of molecule occurs on the keto group and nitro shown the colour indication as red. Colour code range is displayed in between red to yellow. The range of the potential surface is calculated as  $-6.134$  to  $6.134 \text{ e}\text{\AA}^{-1}$  and  $-5.348$  to  $5.348 \text{ e}\text{\AA}^{-1}$ . Red colour indicates more electronegativity as blue indicated electro positivity potential. More negative potential result in more reactive site in the molecular surface. With the accumulation of electron withdrawing groups there are areas of negative potential at the C=O and O-H atoms reliable with having a greater electron density than ring carbon atoms. The addition of electron withdrawing groups produces a large increase in positive potential at the center of the ring. Molecular electrostatic potential are displayed in figure 8. These are visualized by using GaussView5.0.8 molecular visualization.



**Figure - 8: Molecular electrostatic potentials of (a)BDNP and (b) BDNP.**

### 4. CONCLUSION

(1E,4E)-1,5-di-p-tolylpenta-1, 4-dien-3-one and (E)-1-(benzo[d][1,3]dioxol-5-yl)-3-(4-methoxyphenyl)prop-2-en-1-one are successfully synthesized and characterized by spectroscopic studies like FT-IR, FT-Raman and UV-vis. The entire experimental spectrum is supported by theoretical calculations using DFT method. The product formation was confirmed by FT-IR and FT-Raman spectral analyses and the theoretical estimations show minor variations from the experimental vibrational patterns. Electron delocalization is confirmed by MEP. The

intermolecular charge transfer is evidenced by Mulliken charge population analysis.

### 5. REFERENCES

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