

Structural and Vibrational studies (FT-IR, FT-Raman) of Voglibose using DFT calculation

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ABSTRACT. In the present study, we report on the Molecular structure and infrared (IR) and FT-Raman studies of Voglibose (VGB) as well as by calculations based on the density functional theory (DFT) approach; utilizing B3LYP/6-31G(d,p) basis set. The targeted interpretation of the vibrational spectra intended to the basis of calculated potential energy distribution matrix (PED) utilizing VEDA4 program. Stability of the molecule arising from hyperconjugative interactions and charge delocalization was studied using natural bond orbital (NBO) analysis. The results show that change in electron density in the σ^* and π^* antibonding orbitals and E^2 energies confirm the occurrence of intramolecular charge transfer within the molecule. The UV-Visible and NMR spectral analysis were reported by using TD-DFT and gauge GIAO approach respectively and their chemical shifts related to TMS were compared. The lowering of HOMO and LUMO energy gap appears to be the cause for its enhanced charge transfer interactions. Besides, molecular electrostatic potential (MEP) analysis was reported. Due to different potent biological properties, the molecular docking results are also reported.

1. INTRODUCTION

Voglibose is a new and potent in-hibitor of α -glucosidases and is used for the treatment of diabetes mellitus. Voglibose is chemically known as 3,4-Dideoxy-4-[2-hydroxy-1-(hydroxyl methyl) ethyl]amino-2-c-(hydroxymethyl)-D-epinositol has attracted considerable interests due to its wide range of therapeutic and pharma-cological properties, including its excellent inhibitory activity against α -glucosidase and its action against hyperglycemia and various disorders caused by hyper-glycemia [1]. Voglibose obtained from organic synthesis processes is similar to structurally related carbohydrates found naturally [2, 3] and has the empirical formula $C_{10}H_{21}NO_7$. For the treatment of diabetes. It is specifically used for lowering postprandial blood glucose levels thereby reducing the risk of macrovascular complications.

Recently, Iwamoto et al reported [4] Efficacy and safety of vildagliptin and voglibose in Japanese patients with type 2 diabetes: a 12-week, randomized, double-blind, active-controlled study. Mallikarjuna Rao et al [1] presented RP-HPLC method development and validation for estimation of Voglibose in bulk and tablet dosage forms. Determination of voglibose in pharmaceutical formulations by high performance liquid chromatography using refractive index detection given by Karunanidhi Lakshmi et al [5]. Hong Zhang et al [2] reported 1H and ^{13}C NMR analysis of Voglibose and its derivatives. A Comparative Study of Acarbose and Voglibose on Postprandial Hyperglycemia and serum lipids in Type 2 Diabetic patients reported by P. Revathi et al [6].

With the guide of above seen written works, it is clear that there is no quantum mechanical study on this VGB molecule which has propelled to do a definite quantum mechanical investigation for comprehension the vibrational modes, UV-Visible, chemical shifts, HOMO-LUMO, MEP. In this commitment, the structural and vibrational investigations of a basic VGB molecule was introduced and talked about. In the present work we want to focus on vibrational spectrum of the title compound inclusive its interpretation based on the theoretical spectrum calculated by means of

density functional theory (DFT). The redistribution of electron density (ED) in various bonding, antibonding orbitals and $E^{(2)}$ energies have been calculated by natural bond orbital (NBO) analysis to give clear evidence of stabilization originating from the hyperconjugation of various intramolecular interactions.

2. MATERIALS AND METHODS

2.1. FT-IR, FT-Raman and UV-Vis analysis

The compound Voglibose was purchased from Aldrich chemicals, USA and used as such to record the FT-IR and FT-Raman, UV spectra. Bruker IFS 66 V spectrometer was used to record the FT-IR spectrum by KBr pellet method on a equipped with a Globar source, Ge/KBr beam splitter, and a TGS detector in the range of 4000–400 cm^{-1} . The spectral resolution was 2 cm^{-1} . The FT-Raman spectrum was obtained on a Bruker RFS 100/s, Germany and the excitation of the spectrum is with the emission of Nd:YAG laser with a wavelength of 1064 nm, maximal power 150 mW. Cary 500 UV-VIS-NIR spectrometer was used to record the UV absorption spectra associated with Voglibose were examined with the range 200–800 nm. The UV pattern is usually acknowledged from the 10^{-5} molar solution connected with VGB, dissolved with ethanol solvent.

3. COMPUTATIONAL DETAILS

Calculations of the title compound were carried out with the Gaussian 03W program [7] using B3LYP/6-31G(d,p) basis set to predict the molecular structure and vibrational wave numbers and a scaling factor of 0.9608 is used for obtaining a considerably better agreement with experimental data [8,9]. The assignments of the calculated wave numbers are aided by the animation option of the VEDA4 [10] program. The atomic charges, distribution of electron density (ED) in various bonding and antibonding orbitals and stabilization energies, $E^{(2)}$ have been calculated by natural bond orbital (NBO) analysis were performed using NBO 3.1 program [11] as implemented in the Gaussian 03W [7] package at the DFT/B3LYP level of calculation. UV-Visible spectra, electronic transitions, vertical excitation energies and oscillator strengths were computed with the time-dependent DFT method with 6-31G(d,p) basis set in gas phase and using ethanol as solvent. The ^1H and ^{13}C NMR isotropic shielding were calculated with the GIAO method [12] using the optimized parameters obtained from B3LYP/6-31G(d,p) method.

3.1. Prediction of Raman intensities

The Raman activities (S_{Ra}) calculated with Gaussian 03W program [7] converted to relative Raman intensities (I_{Ra}) using the following relationship derived from the intensity theory of Raman scattering [13,14]

$$I_i = \frac{f(v_o - v_i)^4 S_i}{v_i [1 - \exp(-hcv_i / kt)]}$$

Where, v_o is the laser exciting wavenumber in cm^{-1} (in this work, we have used the excitation wavenumber $v_o = 9398.5 \text{ cm}^{-1}$, which corresponds to the wavelength of 1064 nm of a Nd-YAG laser), v_i the vibrational wavenumber of the i^{th} normal mode (cm^{-1}) while S_i is the Raman scattering activity of the normal mode v_i [15].

4. RESULTS AND DISCUSSIONS

4.1. Conformational stability

In order to describe conformational flexibility of the title molecule, the energy profile as a function of N13–C15–C16–O17 torsion angle was achieved with B3LYP/6-31G(d,p) level of calculation as shown in **Fig. 1**. All the geometrical parameters were simultaneously relaxed during the calculations while the N13–C15–C16–O17 torsional angle was varied in steps of 10° , 20° , 30° ... 360° . The energy values obtained from the scan output show that, the structure has a minimum energy (-974.609 Hartree), when the dihedral angle N13–C15–C16–O17 is 0° or 360° (global minimum) and -974.994 Hartree (local minimum) when the dihedral angle N13–C15–C16–O17 is

160°. Therefore, in the present work we have focused on the most stable form of VGB molecule to clarify molecular structure and assignments of vibrational spectra.

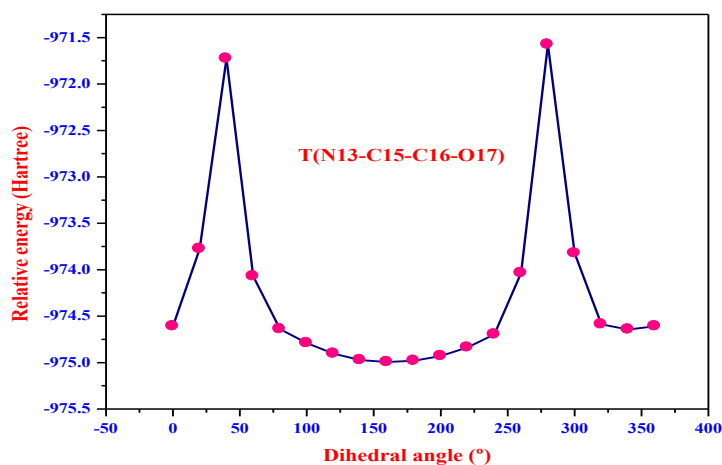


Fig. 1. Dihedral angle-relative energy curves of the Voglibose by B3LYP/6-31G (d,p) level of theory

4.2. Molecular geometry

The optimized geometrical parameters such as bond length, bond angles and dihedral angles calculated by B3LYP/6-31G(d,p) level of calculation using Gaussian 03W program package. To the best of our knowledge, the experimental data on geometric structure of VGB is not available in the literature. Therefore, the theoretical results of VGB have been compared together with closely related molecule 1-Cyclohexylmethoxymethyl-5-[2-hydroxy-1-(hydroxymethyl) ethylamino] cyclohexane-1, 2, 3, 4-tetraol [16] as given in **Table 1**. The C-C bond length of the cyclohexane ring varies from 1.534 Å-1.565 Å. Due to the O-H group substitution on the C1, C2, C3 and C4th position of the cyclohexane ring, the C-C bond lengths are not same for example C1-C2=1.565 Å, C1-C6=1.536 Å, C2-C3=1.544 Å, C3-C4=1.538 Å calculated by DFT method. The C-O bond length on the cyclohexane ring varies from 1.416 Å -1.429 Å by DFT method is good agreement with experimental value 1.429 Å -1.439 Å. The N-H32 bond length is 1019 Å calculated by DFT method. N-C bond lengths are C5-N13=1.481 Å / 1.480 Å, N13-C15=1.480 Å /1.467 Å calculated by DFT/XRD respectively, this result shows good agreement between Theoretical and experimental values. The C-H bond lengths of ethyl alcohol (CH₂OH) group is C11-H29=1.100 Å, C11-H30=1.094 Å and C14-H33=1.092 Å, C14-H34=1.096 Å calculated by DFT method.

As shown in **Fig. 2**, the molecular structure of title compound contains one six-membered ring this ring (from C-1 to C-6) adopt chair conformations. The cyclohexane ring is disordered, with three of the C atoms distributed on two sites with approximately equal occupancy. In addition, one of the hydroxymethyl groups attached to C1 is disordered over the positions. The bond angle at point on the substitution is C2-C1-C6=110.9 °/109.0 ° calculated by DFT/XRD respectively. The unit -N13-C15-C16-O17- connected with C5 by the way of an equatorial bond, and the angles of N13-C5-H22 show 110.9 ° (DFT), C6-C5-N13 show 112.0 ° (DFT), 110.9 ° (XRD) and C4-C5-N13 show 106.2 ° (DFT), 108.9 ° (XRD). The N13-C15-C16 was like a bridge that aligned with cyclohexane ring and CH₂OH.

Dihedral angles of cyclohexane part are found as C1-C2-C3-C4=-50.92 °, C2-C3-C4-C5=53.78 °, C3-C4-C5-C6=-54.98 ° and C4-C5-C6-C1=54.89 °. In case of twist form, the N-atom with the attached carbon 5 was considered are twisted about N13-C5-C6-C1=173.04 ° and C3-C4-C5-N13=-176.63 °. Meanwhile in the molecule, hydrogen bonded N13-H32...O10 appeared in the crystal with a bond length 2.803 (2) Å and bond angle 117.3° [17]. From the theoretical values, we found the idea most of our optimized bond lengths are slightly larger than experimental values due

to be able to fact that the theoretical calculations belong to be able to isolated molecules throughout gaseous phase as well as the experimental results belong for molecules in the solid state.

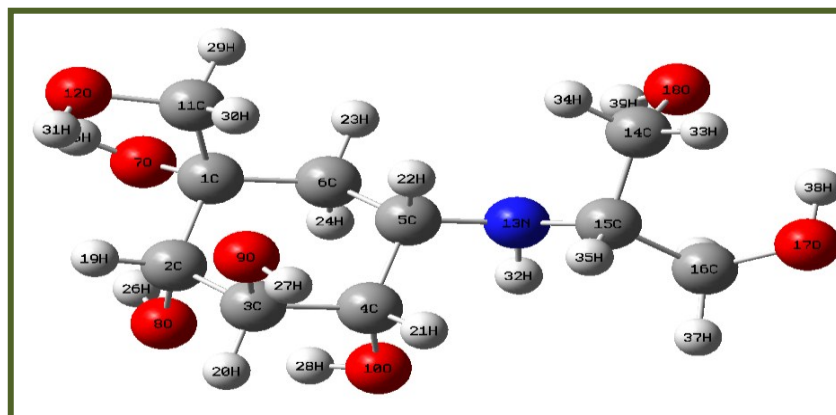


Fig.2. Optimized Molecular structure and atomic numbering of Voglibose

Table 1. Comparison of experimental and theoretical optimized parameter values of the Voglibose [bond length in (Å), angles in (°)]

| Bond length | B3LYP | Exp ^a | Bond angle | B3LYP | Exp ^a | Dihedral angle | B3LYP | Exp ^a |
|-------------|-------|------------------|------------|-------|------------------|----------------|-------|------------------|
| C1-C2 | 1.565 | | C2-C1-C6 | 110.9 | 109.0 | C6-C1-C2-C3 | | 49.45 |
| C1-C6 | 1.536 | | C2-C1-O7 | 110.4 | 109.1 | C6-C1-C2-O8 | | -74.16 |
| C1-O7 | 1.421 | 1.436 | C2-C1-C11 | 111.1 | 106.2 | C6-C1-C2-H19 | | 168.77 |
| C1-C11 | 1.539 | | C6-C1-O7 | 104.7 | 110.9 | O7-C1-C2-C3 | | 165.13 |
| C2-C3 | 1.544 | | C6-C1-C11 | 112.0 | 112.1 | O7-C1-C2-O8 | | 41.51 |
| C2-O8 | 1.416 | 1.431 | O7-C1-C11 | 107.3 | 108.8 | O7-C1-C2-H19 | | -75.54 |
| C2-H19 | 1.094 | | C1-C2-C3 | 113.1 | | C11-C1-C2-C3 | | -75.82 |
| C3-C4 | 1.538 | | C1-C2-O8 | 112.0 | | C11-C1-C2-O8 | | 160.55 |
| C3-O9 | 1.429 | 1.430 | C1-C2-H19 | 107.8 | | C11-C1-C2-H19 | | 43.48 |
| C3-H20 | 1.098 | | C3-C2-O8 | 108.8 | | C2-C1-C6-C5 | | -51.99 |
| C4-C5 | 1.540 | | C3-C2-H19 | 107.9 | | C2-C1-C6-H23 | | -176.27 |
| C4-O10 | 1.428 | 1.429 | O8-C2-H19 | 106.6 | | C2-C1-C6-H24 | | 69.08 |
| C4-H21 | 1.106 | | C2-C3-C4 | 111.9 | | O7-C1-C6-C5 | | -171.12 |
| C5-C6 | 1.534 | | C2-C3-O9 | 109.7 | | O7-C1-C6-H23 | | 64.60 |
| C5-N13 | 1.481 | 1.480 | C2-C3-H20 | 106.3 | | O7-C1-C6-H24 | | -50.04 |
| C5-H22 | 1.101 | | C4-C3-O9 | 109.8 | | C11-C1-C6-C5 | | 72.77 |
| C6-H23 | 1.094 | | C4-C3-H20 | 108.1 | | C11-C1-C6-H23 | | -51.49 |
| C6-H24 | 1.094 | | O9-C3-H20 | 110.7 | | C11-C1-C6-H24 | | -166.14 |
| O7-H25 | 0.969 | | C3-C4-C5 | 112.4 | | C2-C1-O7-H25 | | 72.08 |
| O8-H26 | 0.971 | | C3-C4-O10 | 108.3 | | C6-C1-O7-H25 | | -168.45 |
| O9-H27 | 0.965 | | C3-C4-H21 | 108.1 | | C11-C1-O7-H25 | | -49.19 |
| O10-H28 | 0.973 | | C5-C4-O10 | 109.8 | | C2-C1-C11-O12 | | -66.01 |
| C11-O12 | 1.431 | 1.417 | C5-C4-H21 | 108.5 | | C2-C1-C11-H29 | | 175.37 |
| C11-H29 | 1.100 | | O10-C4-H21 | 109.4 | | C2-C1-C11-H30 | | 54.96 |
| C11-H30 | 1.094 | | C4-C5-C6 | 110.4 | 110.2 | C6-C1-C11-O12 | | 169.32 |
| O12-H31 | 0.964 | | C4-C5-N13 | 106.2 | 108.9 | C6-C1-C11-H29 | | 50.71 |
| N13-C15 | 1.480 | 1.467 | C4-C5-H22 | 107.7 | | C6-C1-C11-H30 | | -69.69 |
| N13-H32 | 1.019 | | C6-C5-N13 | 112.0 | 110.9 | O7-C1-C11-O12 | | 54.81 |
| C14-C15 | 1.533 | | C6-C5-H22 | 109.3 | | O7-C1-C11-H29 | | -63.79 |
| C14-O18 | 1.427 | | N13-C5-H22 | 110.9 | | O7-C1-C11-H30 | | 175.79 |
| C14-H33 | 1.092 | | C1-C6-C5 | 114.0 | | C1-C2-C3-C4 | | -50.92 |
| C14-H34 | 1.096 | | C1-C6-H23 | 108.4 | | C1-C2-C3-O9 | | 71.29 |
| C15-C16 | 1.548 | | C1-C6-H24 | 106.8 | | C1-C2-C3-H20 | | -168.86 |
| C15-H35 | 1.100 | | C5-C6-H23 | 111.0 | | O8-C2-C3-C4 | | 74.43 |
| C16-O17 | 1.411 | | C5-C6-H24 | 109.4 | | O8-C2-C3-O9 | | -163.33 |
| C16-H36 | 1.101 | | H23-C6-H24 | 106.6 | | O8-C2-C3-H20 | | -43.50 |
| C16-H37 | 1.095 | | C1-O7-H25 | 106.0 | | H19-C2-C3-C4 | | -170.15 |
| O17-H38 | 0.969 | | C2-O8-H26 | 107.0 | | H19-C2-C3-O9 | | -47.92 |

| | | | | | |
|---------|-------|-------------|-------|-----------------|---------|
| O18-H39 | 0.968 | C3-O9-H27 | 107.9 | H19-C2-C3-H20 | 71.90 |
| | | C4-O10-H28 | 104.5 | C1-C2-O8-H26 | 79.87 |
| | | C1-C11-O12 | 106.1 | C3-C2-O8-H26 | -46.11 |
| | | C1-C11-H29 | 108.0 | H19-C2-O8-H26 | -162.36 |
| | | C1-C11-H30 | 111.6 | C2-C3-C4-C5 | 53.78 |
| | | O12-C11-H29 | 110.5 | C2-C3-C4-O10 | -67.79 |
| | | O12-C11-H30 | 110.9 | C2-C3-C4-H21 | 173.64 |
| | | H29-C11-H30 | 109.4 | O9-C3-C4-C5 | -68.40 |
| | | C11-O12-H31 | 108.6 | O9-C3-C4-O10 | 170.01 |
| | | C5-N13-C15 | 117.3 | O9-C3-C4-H21 | 51.44 |
| | | C5-N13-H32 | 106.5 | H20-C3-C4-C5 | 170.61 |
| | | C15-N13-H32 | 107.9 | H20-C3-C4-O10 | 49.03 |
| | | C15-C14-O18 | 111.3 | H20-C3-C4-H21 | -69.52 |
| | | C15-C14-H33 | 109.3 | C2-C3-O9-H27 | 163.46 |
| | | C15-C14-H34 | 110.5 | H20-C3-O9-H27 | 46.37 |
| | | O18-C14-H33 | 106.1 | C3-C4-C5-C6 | -54.98 |
| | | O18-C14-H34 | 111.1 | C3-C4-C5-N13 | -176.63 |
| | | H33-C14-H34 | 108.0 | C3-C4-C5-H22 | 64.37 |
| | | N13-C15-C14 | 111.0 | O10-C4-C5-C6 | 65.72 |
| | | N13-C15-C16 | 107.9 | O10-C4-C5-N13 | -55.92 |
| | | N13-C15-H35 | 110.9 | O10-C4-C5-H22 | -174.91 |
| | | C14-C15-C16 | 109.9 | H21-C4-C5-C6 | -174.57 |
| | | C14-C15-H35 | 108.2 | H21-C4-C5-N13 | 63.77 |
| | | C16-C15-H35 | 108.7 | H21-C4-C5-H22 | -55.21 |
| | | C15-C16-O17 | 113.5 | C3-C4-O10-H28 | 158.01 |
| | | C15-C16-H36 | 108.0 | C5-C4-O10-H28 | 34.83 |
| | | C15-C16-H37 | 109.5 | H21-C4-O10-H28 | -84.29 |
| | | O17-C16-H36 | 110.9 | C4-C5-C6-C1 | 54.89 |
| | | O17-C16-H37 | 107.0 | C4-C5-C6-H23 | 177.74 |
| | | H36-C16-H37 | 107.4 | C4-C5-C6-H24 | -64.74 |
| | | C16-O17-H38 | 105.6 | N13-C5-C6-C1 | 173.04 |
| | | C14-O18-H39 | 105.9 | N13-C5-C6-H23 | -64.10 |
| | | | | N13-C5-C6-H24 | 53.41 |
| | | | | H22-C5-C6-C1 | -63.49 |
| | | | | H22-C5-C6-H23 | 59.35 |
| | | | | H22-C5-C6-H24 | 176.86 |
| | | | | C4-C5-N13-C15 | -177.98 |
| | | | | C4-C5-N13-H32 | -56.91 |
| | | | | C6-C5-N13-C15 | 61.40 |
| | | | | C6-C5-N13-H32 | -177.53 |
| | | | | N13-C15-C16-H37 | -79.02 |
| | | | | C14-C15-C16-O17 | 40.10 |
| | | | | C14-C15-C16-H36 | -83.48 |
| | | | | C14-C15-C16-H37 | 159.73 |
| | | | | H35-C15-C16-O17 | -78.21 |
| | | | | H35-C15-C16-H36 | 158.19 |
| | | | | H35-C15-C16-H37 | 41.41 |
| | | | | C15-C16-O17-H38 | -72.23 |
| | | | | H36-C16-O17-H38 | 49.73 |
| | | | | H37-C16-O17-H38 | 166.68 |

4.3. Vibrational assignments

The Voglibose molecule consists of 39 atoms, which undergoes 111 normal modes of vibrations. The molecule belongs to C_1 point group symmetry. On the assumption of C_1 group of symmetry, the 111 fundamental vibrations of the molecule can be distributed as 38 stretching, 75 in-plane bending and 26 out-of plane bending modes. The calculated wavenumbers, observed IR, Raman bands and assignments are given in **Table 2** and their experimental and simulated spectra of IR and Raman are plotted in the **Fig. 3** and **Fig. 4**, respectively.

4.3.1. Cyclohexane ring vibrations

The C-C stretching vibration of the Cyclohexane ring observed the FTIR band at 1070, 892 cm^{-1} and FT-Raman band at 698 cm^{-1} and the computed scaled wavenumbers at 1397, 1070, 895, 698 cm^{-1} by DFT method. These modes are good agreement with literature [18,19]. Guirgis et al.,2012 [20] assigned C-C-C in-plane bending vibration at 450, 349, 354 cm^{-1} by DFT method. In our present work C-C-C in-plane bending vibration observed at 937, 426, 421 cm^{-1} in FTIR spectrum and 440 cm^{-1} in FT-Raman spectrum and theoretically predicted wavenumbers at 939, 444 and 416 cm^{-1} by DFT method, which is good agreement with Cyclohexane derivatives [18,19,20].

The heteroaromatic structure shows the presence of C-H stretching vibration in the region 3100–3000 cm^{-1} which is the characteristics region for the ready identification of C-H stretching vibration [21]. In our present work C-H symmetric and anti symmetric stretching vibrations in ring CH_2 identified at 2988 and 2976 cm^{-1} by DFT calculation. The ring CH_2 anti symmetric stretching vibration observed at 2979 cm^{-1} in FT-Raman spectrum. The computed wavenumbers at 2970, 2948, 2917 and 2816 cm^{-1} by DFT method have been identified as C2-H19, C5-H22, C3-H20 and C4-H21 stretching vibrations respectively. The FTIR band at 1436 and 1233 cm^{-1} have been identified as scissoring and twisting type CH_2 inplane bending vibration in ring respectively and computed wavenumbers at 1449 and 1216 cm^{-1} for this mode. The C-H in-plane bending frequencies occur in the region 1300–1000 cm^{-1} . The out-of-plane bending vibrations are strongly coupled vibration and occur in the region 1000–750 cm^{-1} [22]. In our present work C-C-H in-plane bending vibrations observed at 1263 cm^{-1} in FT-Raman spectrum and the predicted wavenumbers at 1356, 1287, 1286 and 1260 cm^{-1} by DFT method. Mode.nos 78 and 93 has been identified as CH out-of plane bending vibration, which is good agreement with expected values [22].

4.3.2. O-H vibrations

Hydrogen bonding alerts the frequencies of the stretching and bending vibrations. The O-H stretching bands move to lower frequencies usually with increase intensity and band broadening in the hydrogen bonded species. Hydrogen bonding present in five or six member ring system would reduce the O-H stretching bands to 3550 to 3200 cm^{-1} region [23]. Our title molecule contains six O-H groups, so we expect six O-H stretching vibrations. From the Table 2 which is evident that the mode no: 1-7 has been identified as O-H stretching vibrations, these are pure modes and the PED exactly contributes to 100%. The O-H in-plane-bending vibration in phenol, in general, lies in the region 1250 to 1150 cm^{-1} . In our present work, C-O-H in-plane bending vibrations observed at 1070 cm^{-1} in FT-IR spectrum and 1411, 1377 cm^{-1} in FT-Raman spectrum. The calculated wavenumbers at 1415, 1382, 1374, 1371, 1360, 1179, 1168 and 1156 cm^{-1} by DFT method has been identified as C-O-H in-plane bending vibrations. The OH out-of-plane deformation vibration for phenol lies in the 290 to 320 cm^{-1} region for free OH [21]. In our work 4 OH groups directly attached to the Cyclohexane ring. The computed wavenumbers at 463, 438, 279 and 234 cm^{-1} by DFT method has been identified as the O-H out-of plane bending vibrations. Mode no: 63, 66, 68, 70 and 73 has been identified as the O-H out-of plane bending vibrations of the CH_2OH group.

4.3.3. Methylene group vibrations

For the assignments of CH_2 group frequencies, basically six fundamentals vibration can be associated to each CH_2 group namely, CH_2 symmetric stretch, antisymmetric stretch, scissoring and rocking modes, which belong to polarized in-plane vibrations. In addition to that, wagging and twisting mode of CH_2 group would be expected to be depolarized for out-of-plane bending vibration. The asymmetric CH_2 stretching vibration generally observed in the region 3000–2900 cm^{-1} , while the CH_2 symmetric stretch will appear between 2900 cm^{-1} and 2800 cm^{-1} [24]. For title molecule CH_2 anti symmetric and symmetric stretching vibrations observed at 2979, 2889 cm^{-1} and 2895 cm^{-1} in FT-Raman and FT-IR spectrum respectively. The computed wavenumbers at 3001, 2976 and 2963 cm^{-1} and 2988, 2888, 2882 and 2876 cm^{-1} are assigned as CH_2 anti symmetric and symmetric stretching vibrations. The CH_2 scissoring vibrations appear normally in the region 1490–

1435 cm^{-1} as medium intense bands [25]. In our present investigation FT-Raman band at 1460 cm^{-1} and computed wavenumbers at 1465, 1464 and 1457 cm^{-1} have been identified as CH_2 scissoring vibrations. Absorption of hydrocarbons due to CH_2 twisting and wagging vibration is observed in the 1350-1150 cm^{-1} region [26]. For title molecule the FT-IR band at 1233 cm^{-1} and 1216 cm^{-1} by DFT calculation gives the CH_2 twisting vibrations. Mode no: 53 have been identified as the CH_2 Rocking mode.

4.3.4. N-H and C-N vibrations

The N-H stretching vibrations generally give rise to bands at 3500–3400 cm^{-1} [27]. For title molecule N-H stretching vibration observed at 3254 cm^{-1} in FT-Raman spectrum and computed at 3334 cm^{-1} by DFT method. The observed FT-Raman band at 3254 cm^{-1} and calculated scaled wavenumber at 3334 is cm^{-1} is red shifted by 146 cm^{-1} and 66 cm^{-1} respectively. The reason for this long deviation is due to presence of the N13–H32...O10 intra molecular interaction. This red shifting is got enhanced by the reduction in the N-H bond values occurring in the hydrogen bonding interactions. The CNH vibration where N and H atoms move in the same direction relative to the carbon atom gives rise to a weaker band [25] near 1250 cm^{-1} . In our present study the theoretically predicted wave number at 1458 cm^{-1} gives the CNH in-plane bending vibration.

Silverstein et al., [26] assigned the C-N stretching absorption in the region 1382 to 1286 cm^{-1} for aromatic amines. For title molecule C-N stretching vibration observed at 1134 cm^{-1} in FT-IR spectrum and 1136 and 1086 cm^{-1} in FT-Raman spectrum. The calculated wave numbers at 1135 and 1087 cm^{-1} has been identified as C-N stretching vibration, which is good agreement with experimental values. The calculated scaled wavenumber at 505 cm^{-1} by DFT method gives CNC in-plane bending vibrations. The observed FT-Raman band at 377 cm^{-1} and computed wave number at 379 cm^{-1} by DFT method has been identified as CCNC out-of plane bending vibration.

4.3.5. C-O vibrations

The C–O stretching vibration in phenol occurs as a strongest band in the region 1300 to 1200 cm^{-1} [28]. For title molecule C-O stretching vibration observed at 1026 cm^{-1} in FT-IR spectrum and 1047 cm^{-1} in FT-Raman spectrum. The calculated wavenumbers by DFT method at 1100, 1063, 1057, 1049, 1045, 1032 and 1008 cm^{-1} are assigned C-O stretching vibrations. The observed FT-Raman band at 630 cm^{-1} and theoretically predicted wavenumbers at 649, 629, 333, 331, 316 and 234 cm^{-1} are identified as C-C-O in-plane bending vibrations. The C-C-C-O out-of plane bending vibration observed at 397 cm^{-1} in FT-Raman band and calculated wavenumbers at 398, 339, and 251 cm^{-1} by DFT calculation. Mode nos: 105-109 has been identified as C-C-C-O torsional modes.

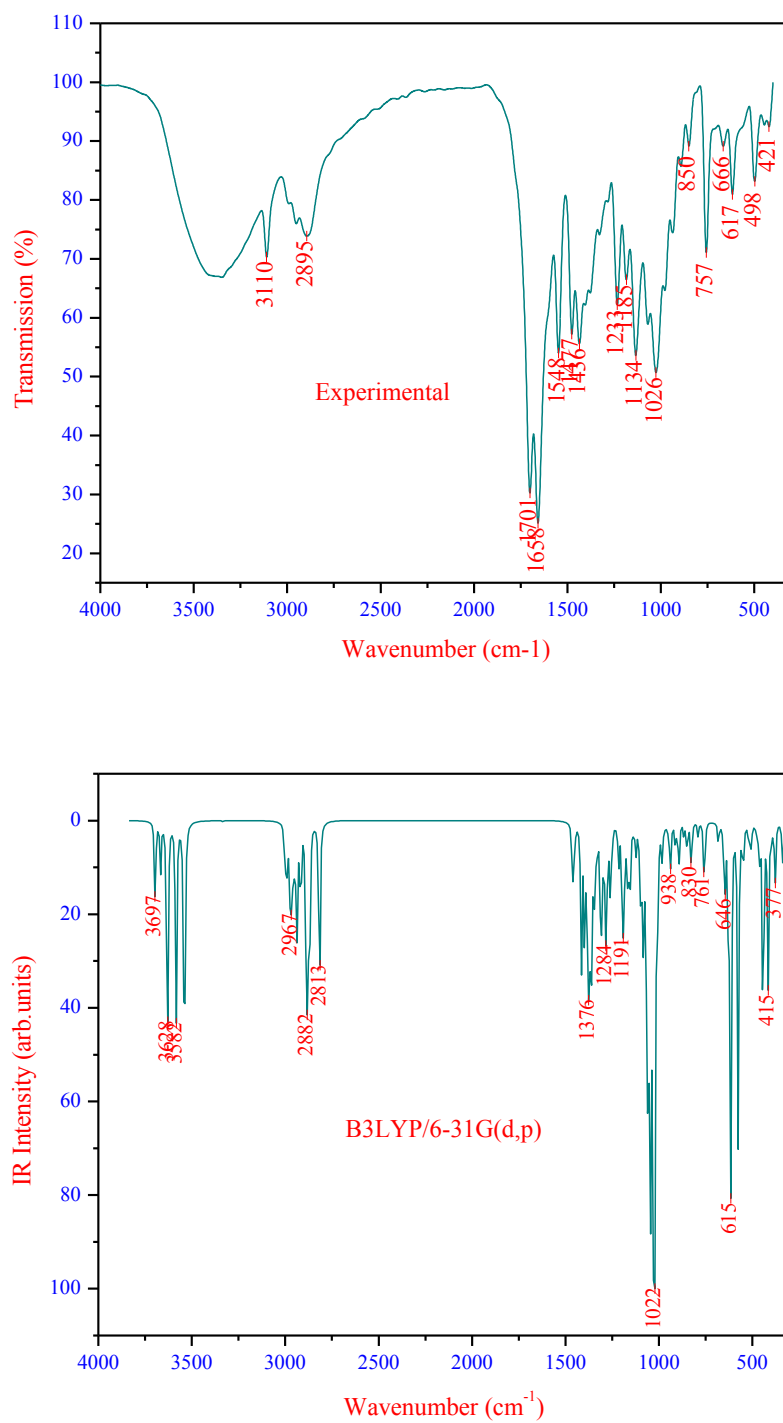


Fig. 3. Comparison of experimental and theoretical B3LYP/6-31G(d,p) FT-IR spectrum for Voglibose

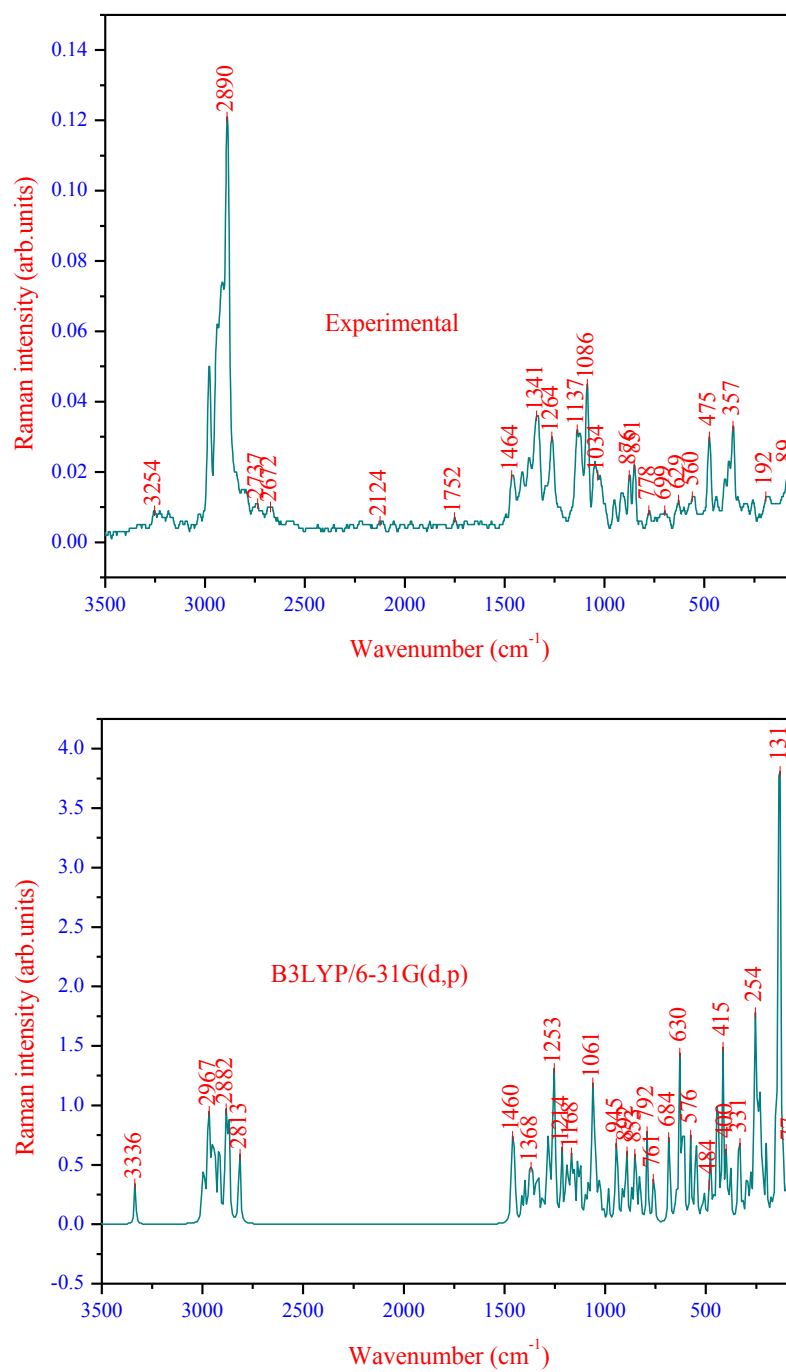


Fig.4. Comparison of experimental and theoretical B3LYP/6-31G(d,p) FT-Raman spectrum for Voglibose

Table 2. Comparison of the experimental and calculated vibrational spectra and proposed assignments of Voglibose

| Mode No | Experimental wave numbers/cm ⁻¹ | | Theoretical wave numbers/cm ⁻¹ | | | | Vibrational assignments with PED (≥10%) |
|---------|--|----------|---|--------|------------------------------|------------------------------|--|
| | FT-IR | FT-Raman | B3LYP/6-31G(d,p) | | | | |
| | | | Unscaled | scaled | I _{IR} ^a | I _{Ra} ^b | |
| 1 | | | 3846 | 3695 | 44.46 | 3.09 | V _{O12H31} (100) |
| 2 | | | 3816 | 3666 | 33.39 | 2.82 | V _{O9H27} (100) |
| 3 | | | 3784 | 3636 | 31.97 | 1.67 | V _{O18H39} (100) |
| 4 | | | 3779 | 3631 | 51.69 | 2.45 | V _{O7H25} (100) |
| 5 | | | 3775 | 3627 | 49.99 | 1.87 | V _{O17H38} (100) |
| 6 | | | 3730 | 3584 | 72.26 | 1.33 | V _{O18H39} (100) |
| 7 | | | 3684 | 3540 | 90.59 | 2.65 | V _{O8H26} (100) |
| 8 | | 3254 | 3470 | 3334 | 4.93 | 2.95 | V _{N13H32} (98) |
| 9 | | | 3123 | 3001 | 37.79 | 3.89 | V _{C14H33} (96) anti.sym CH2 |
| 10 | | | 3110 | 2988 | 32.98 | 2.82 | V _{C6H23} (64)sym in ring CH2 |
| 11 | | 2979 | 3097 | 2976 | 33.48 | 3.00 | V _{C6H24} (32)ant.sym in ring CH2 |
| 12 | | | 3091 | 2970 | 34.62 | 4.93 | V _{C2H19} (93) |
| 13 | | | 3084 | 2963 | 45.7 | 4.22 | V _{C11H29} (68)ant.sym in CH2 |
| 14 | 2951 | | 3068 | 2948 | 40.31 | 5.38 | V _{C5H22} (47) in ring |
| 15 | | | 3055 | 2935 | 49.46 | 3.39 | V _{C5H22} (46) in ring |
| 16 | | 2912 | 3036 | 2917 | 48.4 | 5.54 | V _{C3H20} (73) in ring |
| 17 | 2895 | 2889 | 3006 | 2888 | 49.19 | 2.89 | V _{C16H36} (91) sym in CH2 |
| 18 | | | 3000 | 2882 | 54.89 | 4.62 | V _{C11H9} (95)sym in CH2 |
| 19 | | | 2993 | 2876 | 44.4 | 3.63 | V _{C14H34} (91)sym in CH2 |
| 20 | | | 2985 | 2868 | 47.69 | 4.85 | V _{C15H35} (93) |
| 21 | | | 2931 | 2816 | 71.28 | 5.33 | V _{C4H21} (93) in ring |
| 22 | | | 1525 | 1465 | 18.85 | 4.93 | δ _{sciH36C16H37} (56) |
| 23 | | | 1524 | 1464 | 22.43 | 5.48 | δ _{sciH33C14H34} (56) |
| 24 | | | 1518 | 1458 | 29.11 | 3.61 | δ _{H32N13C15} (63) |
| 25 | | 1460 | 1516 | 1457 | 20.99 | 7.64 | δ _{sciH36C16H37} (56) |
| 26 | 1436 | | 1508 | 1449 | 17.22 | 5.98 | δ _{sciH23C6H24} (84) in Ring+ γ _{C11C1012H30} (42) |
| 27 | | 1411 | 1473 | 1415 | 58.17 | 4.35 | δ _{H28O10C4} (55)+ γ _{C4C5O10H21} (28) |
| 28 | | | 1458 | 1401 | 21.16 | 4.65 | δ _{H26O8C2} (20)+ γ _{C3C4O9H20} (10) |
| 29 | | | 1454 | 1397 | 52.62 | 4.47 | V _{C2C3} (11) in ring+ δ _{H27O9C3} (14) |
| 30 | | | 1438 | 1382 | 46.56 | 3.83 | δ _{H25O7C1} (21)+ γ _{C14H33C15H34} (20) |
| 31 | | 1377 | 1430 | 1374 | 43.12 | 2.51 | δ _{H38O17C16} (32)+γ _{C16C15O17H36} (11)+ τ _{H37C16C15C14} (14) |
| 32 | | | 1428 | 1372 | 52.23 | 7.79 | δ _{H36C16O17} (41) |
| 33 | | | 1419 | 1363 | 45.79 | 4.09 | δ _{H38O17C16} (20) |
| 34 | | | 1416 | 1360 | 35.84 | 4.04 | δ _{H27C3O9} (45) |
| 35 | | | 1411 | 1356 | 33.92 | 4.11 | δ _{H22C5C6} (24) |
| 36 | | | 1399 | 1344 | 39.13 | 4.85 | δ _{H29C11O12} (35) |
| 37 | 1329 | 1334 | 1388 | 1334 | 27.87 | 7.85 | δ _{H20C3O9} (37)+ γ _{C15C16N13H35} (30) |
| 38 | | | 1368 | 1314 | 40.48 | 3.71 | δ _{H25O7C1} (29)+ γ _{C5C6N13H22} (36) |
| 39 | | | 1358 | 1305 | 51.23 | 3.73 | δ _{H25O7C1} (29)+ γ _{C5C6N13H22} (36) |
| 40 | | | 1339 | 1287 | 29.93 | 7.98 | δ _{H21C4C5} (37) |
| 41 | | | 1338 | 1286 | 48.2 | 6.00 | δ _{H22C5C6} (11)+ γ _{C5C6N13H22} (10)+ τ _{H24C6C5C4} (13) |
| 42 | | | 1326 | 1274 | 35.09 | 6.99 | τ _{C2H19O8H26} (40) |
| 43 | | 1263 | 1311 | 1260 | 37.6 | 6.66 | δ _{H22C5C6} (13) |
| 44 | | | 1307 | 1256 | 17.37 | 9.09 | δ _{H29C11H30} (43) |
| 45 | | | 1301 | 1250 | 20.21 | 11.09 | γ _{C4C5O10H21} (14) |
| 46 | 1233 | | 1266 | 1216 | 32.67 | 9.10 | δ _{twistH29C11H30} (33)+ δ _{twistH23C6H24} (43) in ring |
| 47 | | | 1244 | 1195 | 51.12 | 5.88 | δ _{H19C2C3} (20)+ γ _{C4C5O10H21} (11) |
| 48 | 1185 | | 1236 | 1188 | 47.36 | 7.95 | δ _{H23C6C1} (15)+ γ _{C3C4O9H20} (16) |
| 49 | | | 1227 | 1179 | 15.77 | 4.51 | δ _{H39O18C14} (15) |
| 50 | | | 1216 | 1168 | 33.03 | 7.59 | δ _{H33C14O18} (39) |
| 51 | | | 1203 | 1156 | 48.55 | 8.98 | δ _{H31C11O12} (59) |
| 52 | 1134 | 1136 | 1181 | 1135 | 10.62 | 9.19 | V _{N13C5} (11) |
| 53 | | | 1169 | 1123 | 25.65 | 7.53 | δ _{rockH29C11H30} (59) |
| 54 | | | 1145 | 1100 | 37.97 | 4.75 | V _{O10C4} (11) |

| | | | | | | | |
|-----|------|------|------|------|-------|--------|--|
| 55 | | 1087 | 1131 | 1087 | 59.4 | 6.92 | $\nu_{N13C5(23)}$ |
| 56 | 1070 | | 1114 | 1070 | 42.99 | 7.10 | $\nu_{C2C3(16)+\delta_{H31O12C11(11)}}$ |
| 57 | | | 1106 | 1063 | 69.69 | 11.34 | $\nu_{O17C16(61)}$ |
| 58 | | | 1100 | 1057 | 56.01 | 10.12 | $\nu_{O7C1(14)}$ |
| 59 | | | 1092 | 1049 | 61.85 | 6.56 | $\nu_{O12C11(13)}$ |
| 60 | | 1047 | 1088 | 1045 | 75.34 | 4.86 | $\nu_{O9C3(46)}$ |
| 61 | | | 1075 | 1033 | 23.11 | 5.88 | $\nu_{O8C2(30)}$ |
| 62 | 1026 | | 1074 | 1032 | 100 | 4.33 | $\nu_{O8C2(21)}$ |
| 63 | | | 1063 | 1021 | 97.92 | 5.42 | $\nu_{O18C14(16)+\gamma_{C14C15O18H33}}$ |
| 64 | | | 1049 | 1008 | 39.34 | 3.56 | $\nu_{O12C11(16)}$ |
| 65 | 978 | | 1024 | 984 | 26.31 | 6.52 | $\nu_{O10C4(21)}$ |
| 66 | | 950 | 986 | 947 | 19.54 | 10.86 | $\gamma_{C16C15O17H36(28)}$ |
| 67 | 937 | | 977 | 939 | 31.25 | 7.71 | $\delta_{C2C3C4(11)}$ |
| 68 | | 914 | 949 | 912 | 25 | 7.79 | $\nu_{N13C15(10)+\delta_{C2C3C4(20)+\gamma_{C14C15O18H33(27)}}$ |
| 69 | 892 | | 931 | 895 | 37.29 | 12.21 | $\nu_{C4C5(12)}$ |
| 70 | | 874 | 902 | 867 | 17.85 | 7.14 | $\nu_{O7C1(30)+\gamma_{C11C10I2H30(16)}}$ |
| 71 | 850 | 850 | 885 | 850 | 29.51 | 13.00 | $\nu_{C14C15(10)+\gamma_{N13C5C15H32(10)}}$ |
| 72 | | | 861 | 827 | 37.33 | 10.10 | $\gamma_{N13C5C15H32(30)+\nu_{C14C15(40)}}$ |
| 73 | | 776 | 823 | 791 | 18.39 | 12.63 | $\nu_{C14C15(38)+\gamma_{N13C5C15H32(39)+\gamma_{C16C15O17H36(10)}}$ |
| 74 | 757 | | 789 | 758 | 44.32 | 11.32 | $\nu_{C1C11(22)}$ |
| 75 | | 698 | 710 | 682 | 22.84 | 15.04 | $\nu_{C4C5(20)}$ |
| 76 | | | 675 | 649 | 46.35 | 8.51 | $\delta_{C1C11O12(21)}$ |
| 77 | | 630 | 655 | 629 | 46.57 | 20.00 | $\delta_{C1C11O12(31)}$ |
| 78 | 617 | | 641 | 616 | 94.83 | 10.36 | $\gamma_{H23C6C5C4(12)}$ |
| 79 | | | 634 | 609 | 33.63 | 14.57 | $\tau_{H28O10C4C3(51)}$ |
| 81 | | 553 | 571 | 549 | 35.45 | 18.29 | $\tau_{H39O18C14C15(21)}$ |
| 82 | | | 539 | 518 | 23.93 | 7.77 | $\delta_{C16C15N13(31)}$ |
| 83 | | | 526 | 505 | 24.88 | 9.01 | $\delta_{C5N13C15(10)+\tau_{H39O18C14C15(11)}}$ |
| 84 | 480 | 475 | 499 | 479 | 13.98 | 16.75 | $\gamma_{C11C2C6C1(11)}$ |
| 85 | | | 482 | 463 | 31.8 | 8.22 | $\gamma_{H28O10C4C5(11)}$ |
| 86 | 446 | 440 | 462 | 444 | 65.76 | 20.07 | $\delta_{C2C1C6(11)}$ |
| 87 | | | 456 | 438 | 34.99 | 14.46 | $\gamma_{H25O7C1C6(11)}$ |
| 88 | 421 | | 433 | 416 | 62.42 | 24.67 | $\delta_{C3C4C5(13)}$ |
| 89 | | 397 | 414 | 398 | 20.04 | 16.66 | $\gamma_{C1C6C11O7(21)}$ |
| 90 | | 377 | 394 | 379 | 40.8 | 15.22 | $\delta_{C14C15N13(19)+\gamma_{C16C14N13C15(16)}}$ |
| 91 | | | 353 | 339 | 30.23 | 15.53 | $\delta_{C1C2O8(31)+\tau_{H31O12C11C1(73)+\gamma_{C1C6C11O7(11)}}$ |
| 92 | | | 345 | 331 | 15.18 | 18.14 | $\delta_{C6C1O7(19)}$ |
| 93 | | | 329 | 316 | 5 | 8.16 | $\delta_{C5C4O10(14)+\gamma_{H23C6C5C4(10)}}$ |
| 94 | | | 308 | 296 | 24.68 | 18.69 | $\delta_{C2C3O9(19)+\gamma_{C11C2C6C1(20)}}$ |
| 95 | | | 290 | 279 | 16.21 | 15.52 | $\gamma_{H27O9C3C2(58)}$ |
| 96 | | 257 | 271 | 260 | 15.2 | 20.30 | $\tau_{C15C14O18H39(46)}$ |
| 97 | | | 261 | 251 | 74.46 | 40.47 | $\gamma_{C4C3C5O10(10)}$ |
| 98 | | | 244 | 234 | 45.48 | 33.89 | $\delta_{C15C14O18(16)+\gamma_{H26O8C3C2(48)}}$ |
| 99 | | | 235 | 226 | 11.65 | 15.78 | $\gamma_{C11C2C6C1(17)}$ |
| 100 | | | 227 | 218 | 20.99 | 16.53 | $\delta_{C6C1C11(28)}$ |
| 101 | | | 208 | 200 | 18.72 | 22.95 | $\delta_{C2C3O9(13)+\tau_{C3C2C1C6(12)}}$ |
| 102 | | 178 | 182 | 175 | 12.38 | 11.85 | $\tau_{C1C2C3O9(35)}$ |
| 103 | | | 157 | 151 | 54.09 | 34.87 | $\tau_{O31C1C11O12(55)}$ |
| 104 | | | 140 | 135 | 64.73 | 100.00 | $\delta_{C5N13C15(20)}$ |
| 105 | | | 123 | 118 | 12.2 | 21.49 | $\tau_{C16C15C14O18}$ |
| 106 | | | 98 | 94 | 13.97 | 24.33 | $\tau_{C14C15C16O38(45)}$ |
| 107 | | | 95 | 91 | 15.09 | 17.58 | $\tau_{C14C15C18O39(49)}$ |
| 108 | | 86 | 83 | 80 | 3.16 | 21.65 | $\tau_{C14C15C16O17(38)}$ |
| 109 | | | 75 | 72 | 8.34 | 46.95 | $\tau_{C6C1C11O12(55)}$ |
| 110 | | | 42 | 40 | 14.13 | 46.18 | $\delta_{C5N13C15(15)+\tau_{C5N13C15C14(44)}}$ |
| 111 | | | 40 | 38 | 6.65 | 48.75 | $\tau_{C6C5N13C15(57)}$ |

v-stretching; δ -in-plane-bending; γ -out-of-plane bending; τ -torsion; w-weak; s-strong; vs-very strong; vw-very weak; m-medium.

^a I_{IR} -IR Intensity ($Kmmol^{-1}$);

^b I_{Ra} -Raman intensity (Arb units) (intensity normalized to 100%).

4.4. NBO analysis

In the NBO analysis [29], all possible interactions between “filled” (donor) Lewis-type NBOs and “empty” (acceptor) non-Lewis NBOs were investigated. The energies of these interactions were calculated second-order perturbation theory. These interactions (or energetic stabilizations) are named as ‘delocalization’ corrections to the zeroth-order natural Lewis structure. For each donor NBO (i) and acceptor NBO (j); the stabilization energy E associated with i→j delocalization, is explicitly estimated by the following equation:

$$E_2 = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$

where q_i is the donor orbital occupancy, ε_i and ε_j diagonal elements and $F(i,j)$ is the off diagonal NBO Fock matrix element.

The interactions σ (C2-H19) → σ^* (C1-C6) and σ^* (C3-C4) having the stabilization energy is 3.08, 3.27 KJ mol⁻¹ and σ (C3-H20) → σ^* (C1-C2) having the stabilization energy is 3.24 KJ mol⁻¹ are responsible for conjugation of respective σ -bonds in Cyclohexane ring (**Table 3**). The intramolecular interaction is formed by the orbital overlap between LP(1)N13→ π^* (O10-H28) bond orbital, which results intramolecular charge transfer causing stabilization energy 4.86 KJ mol⁻¹ of the system. The energy contribution of LP(2)O17→ π^* (C15-C16), LP(2)O18→ π^* (C15-H35), LP(2)O10→ π^* (C4-H21) are 9.07, 6.38, 7.65 KJ mol⁻¹, respectively, and hence there is a possibility for delocalization of lone pair (LP) of electrons between O17 and C15-C16 and O10 and C4-H21.

Table 3. Second order Perturbation theory analysis of Fock Matrix in NBO basis for Voglibose.

| Donor (i) | E _D (i)(e) | Acceptor(j) | E _D (j)(e) | E ⁽²⁾ ^a KJ mol ⁻¹ | E(j)-E(i) ^b a.u | F(i,j) ^c a.u |
|-------------------|-----------------------|--------------------|-----------------------|--|----------------------------|-------------------------|
| σ (C2-H19) | 1.973 | σ^* (C1-C6) | 0.029 | 3.08 | 0.87 | 0.046 |
| | | σ^* (C3-C4) | 0.041 | 3.27 | 0.85 | 0.047 |
| σ (C3-H20) | 1.978 | σ^* (C1-C2) | 0.070 | 3.24 | 0.86 | 0.048 |
| | | π^* (C1-C2) | 0.070 | 8.65 | 0.63 | 0.066 |
| LP(2)O7 | 1.947 | RY*(1)C1 | 0.008 | 4.29 | 1.52 | 0.072 |
| LP(1)O7 | 1.976 | π^* (C1-C11) | 0.043 | 4.22 | 0.64 | 0.046 |
| LP(1)O8 | 1.977 | RY*(1)C2 | 0.007 | 3.36 | 1.38 | 0.061 |
| LP(2)O8 | 1.946 | π^* (C1-C2) | 0.070 | 9.09 | 0.62 | 0.067 |
| LP(2)O8 | 1.946 | π^* (C2-C3) | 0.015 | 3.86 | 0.63 | 0.044 |
| LP(2)O9 | 1.957 | π^* (C3-C4) | 0.042 | 7.40 | 0.67 | 0.063 |
| LP(2)O9 | 1.957 | π^* (C3-H20) | 0.026 | 3.72 | 0.76 | 0.048 |
| LP(1)O10 | 1.974 | RY*(1)C4 | 0.007 | 3.13 | 1.49 | 0.061 |
| LP(1)O10 | 1.974 | π^* (C4-C5) | 0.038 | 3.97 | 0.92 | 0.054 |
| LP(2)O10 | 1.941 | π^* (C4-H21) | 0.034 | 7.65 | 0.77 | 0.069 |
| LP(2)O10 | 1.941 | π^* (O8-H26) | 0.028 | 7.14 | 0.84 | 0.069 |
| LP(2)O12 | 1.965 | π^* (C11-H29) | 0.026 | 5.22 | 0.75 | 0.056 |
| LP(2)O12 | 1.965 | π^* (C11-30) | 0.027 | 5.50 | 0.77 | 0.058 |
| LP(1)N13 | 1.908 | π^* (C5-H22) | 0.032 | 6.31 | 0.76 | 0.063 |
| LP(1)N13 | 1.908 | π^* (O10-H28) | 0.027 | 4.86 | 0.76 | 0.055 |
| LP(1)N13 | 1.908 | π^* (C14-C15) | 0.040 | 3.46 | 0.69 | 0.044 |
| LP(1)N13 | 1.908 | π^* (C15-H35) | 0.028 | 4.21 | 0.76 | 0.051 |
| LP(2)O17 | 1.948 | π^* (C15-C16) | 0.039 | 9.07 | 0.65 | 0.069 |
| LP(2)O17 | 1.948 | π^* (C16-H36) | 0.028 | 4.43 | 0.72 | 0.051 |
| LP(2)O18 | 1.954 | π^* (C14-H34) | 0.023 | 4.83 | 0.67 | 0.051 |
| LP(2)O18 | 1.954 | π^* (C15-H35) | 0.028 | 6.38 | 0.77 | 0.063 |

4. 5. Electronic properties

4.5.1. UV-Visible spectral analysis

The experimental UV–Visible electronic absorption maxima (λ_{max}) of Voglibose recorded in ethanol together with the theoretical results involving the vertical excitation energies, oscillator strength (f) and wavelength at maximum absorption calculated at B3LYP/ 6-31G(d,p) basis set in gas phase and in ethanol solvent are given in **Table 4**. The experimental UV-Vis spectrum of the title compound is shown in **Fig. 5**. Due to the Frank–Condon principle, the maximum absorption peak (λ_{max}) in an UV–visible spectrum corresponds to vertical excitation. The B3LYP/6-31G(d,p) calculations (in ethanol) predict two intense electronic transitions at 7.2622 eV (270.73 nm) with an oscillator strength $f = 0.0014$ and other one 7.5971 eV (234.44 nm) with an oscillator strength $f = 0.0103$, which are in good agreement with the measured experimental data (261 and 227 nm).

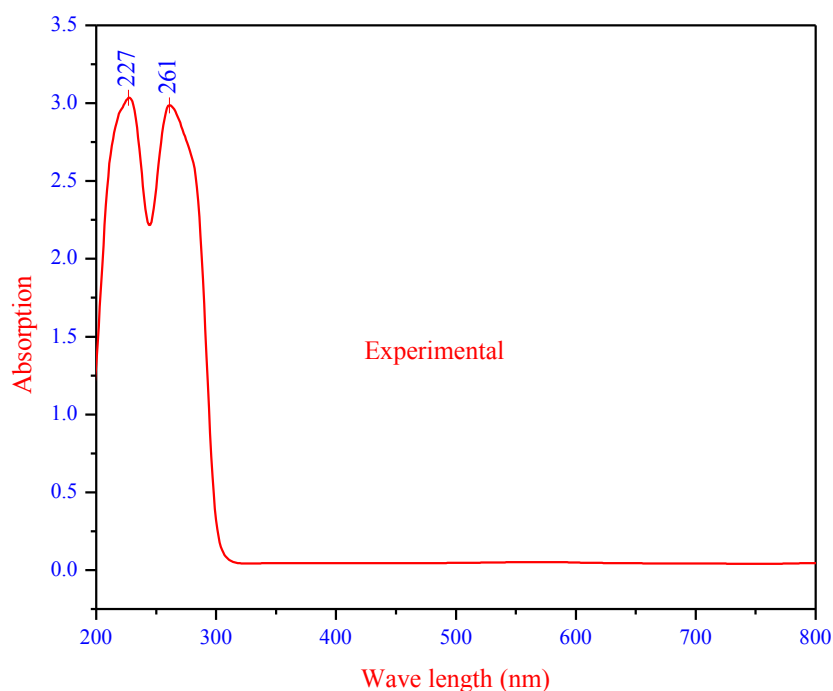


Fig. 5. UV-Visible spectrum (Ethanol) of Voglibose

Table 4. The experimental and computed absorption wavelength λ (nm), excitation energies E (eV), absorbance and oscillator strengths (f) of Voglibose in Ethanol solution and gas phase

| Experimental | | TD-DFT/B3LYP/6-31G(d,p) | | | | | |
|----------------|--------|-------------------------|--------|--------|----------------|--------|--------|
| Ethanol | | Ethanol | | | Gas | | |
| λ (nm) | Abs. | λ (nm) | E(eV) | f(a.u) | λ (nm) | E(eV) | f(a.u) |
| 261 | 2.9868 | 270.73 | 7.2622 | 0.0163 | 268.84 | 6.9325 | 0.0014 |
| 227 | 3.0363 | 223.20 | 7.5971 | 0.0006 | 234.44 | 7.1077 | 0.0103 |
| - | - | 160.52 | 7.7240 | 0.0404 | 170.09 | 7.2894 | 0.0026 |

4.5.2. HOMO-LUMO Analysis

The highest occupied molecular orbital (HOMO) is the orbital that primarily acts as an electron donor and the lowest unoccupied molecular orbital (LUMO) is the orbital that largely acts as the electron acceptor. The frontier orbital energy gap helps characterize the chemical reactivity

and kinetic stability of the molecule. According to **Fig. 6**, the HOMO is spread heavily over the Cyclohexane ring region and LUMO is spread over the entire molecule. For title molecule the calculated HOMO energy is -6.3460 eV and LUMO energy is 1.1263 eV and the HOMO-LUMO energy gap is 5.2179 eV.

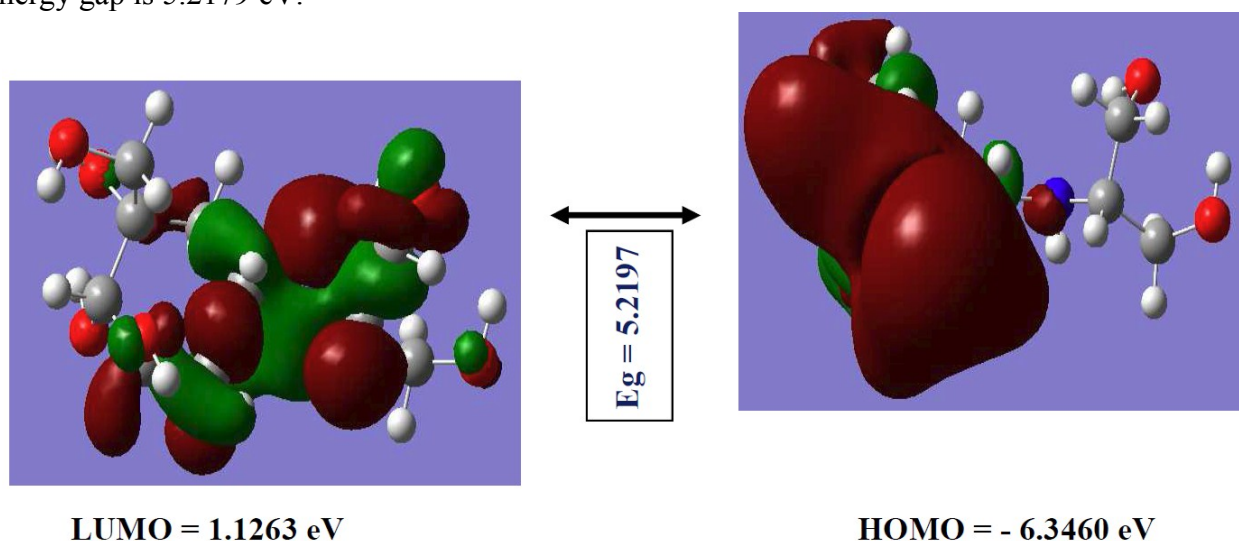


Fig.6. The atomic orbital compositions of the frontier molecular orbital for Voglibose

4.5.3. Molecular Electrostatic Potential (MEP) Analysis

In order to grasp the molecular interactions, the molecular electrostatic potentials (MEPs) are used. Recently, the MEPs have been used for interpreting and predicting relative reactivities sites for electrophilic and nucleophilic attack, investigation of biological recognition, hydrogen bonding interactions, studies of molecular cluster, crystal behavior, correlation and prediction of a wide range of macroscopic properties [30]. The MEP diagram (front and back view) of the voglibose molecule is shown in **Fig. 7**. The color scheme for the MEP surface will be partially negative charge or maybe red-electron rich; partially positive charge or maybe blue-electron deficient; yellow slightly electron packed region; light blue-slightly electron deficient region, Additionally, green color parts represent also regions of zero potential respectively. For the title molecule yellow color represents the electron packed region which is mostly cover the oxygen atoms and also the positive region is actually over the NH group. Green color represents the zero potential regions mostly over the all protons.

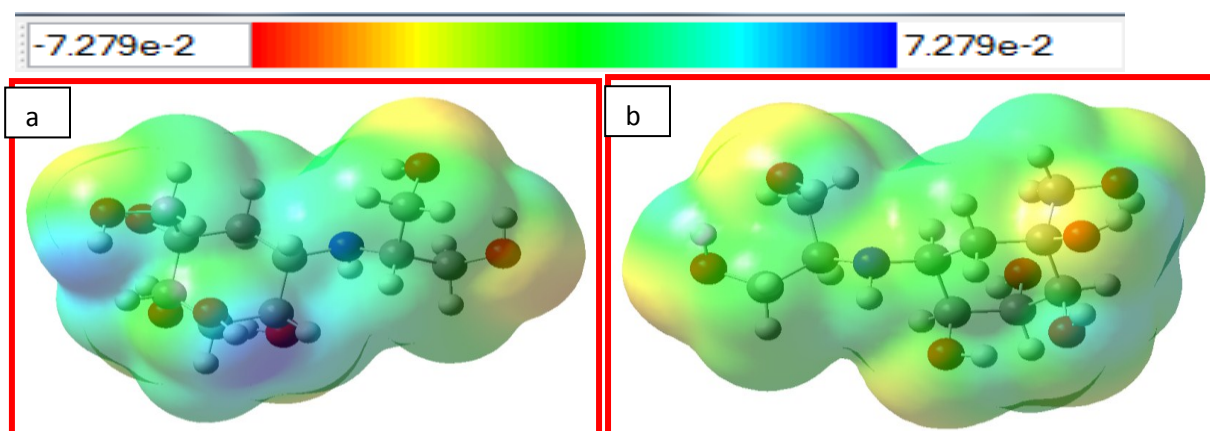


Fig.7. a) Front view b) back view of Molecular electrostatic Potential map (MEP) for Voglibose

4.6. NMR spectral Analysis

NMR spectroscopy has proved to be an exceptional tool to elucidate structure and molecular conformation. The “gauge-independent atomic orbital” (GIAO) method [31] has proven to be quite accepted and accurate, in particular when applied in the context of highly correlated abinitio methods. The ^1H and ^{13}C theoretical and experimental [2] (water solvent) chemical shifts, isotropic shielding constants and the assignments of voglibose are also given in the **Table 5**. Taking into account that the range of ^{13}C NMR chemical shift for analogous organic molecules usually is >100 ppm [32]. The chemical shift of C1,C2,C3,C4 carbon peaks in the rings attached to oxygen atom are observed from 17.10 ppm to 76.28 ppm are calculated from 69.54 ppm to 70.59 ppm at B3LYP/6-31G(d,p) level of theory. For title molecule ^{13}C chemical values of these carbon atoms are down shifted from the expected values. The reason for the down shift is due to the substitution of oxygen and carbon atoms for C1 atom and oxygen and hydrogen atoms for C2, C3, and C4 atom respectively. Due to the double proton substitution C6 atom get down shifted, the observed / calculated value is 29.34 ppm/28.96 ppm. Similarly, due to electro negative oxygen atom substitution causes C11, C14 and C16 atoms gets down shielding shown in Table 5.

Hydrogen attached or nearby electron donating atom or group increases the shielding and moves the resonance towards to a lower frequency. The chemical shifts obtained and calculated for the hydrogen atoms of methyl groups are quite low. All values are ≤ 3 ppm [33] due to shielding effect. In our present study ethylene group chemical shift values of protons H23 and H24 is 1.36/1.01, 1.89/1.48 (Experimental/calculated). Due to electro negative oxygen bonding causes H25-H28 have the low chemical shift values, which are calculated from 2.29-2.86 ppm by DFT method.

Table 5. Table predicted ^1H and ^{13}C NMR isotropic chemical shifts (with respect to TMS, all values in ppm) for Voglibose

| ^{13}C NMR | | | ^1H NMR | | |
|---------------------|--------------|-------|------------------|--------------|-------|
| Atom position | Experimental | B3LYP | Atom position | Experimental | B3LYP |
| C1 | 74.10 | 69.54 | H19 | 3.67 | 3.69 |
| C2 | 65.19 | 66.38 | H20 | | 4.01 |
| C3 | 72.07 | 67.65 | H21 | 3.48 | 3.38 |
| C4 | 76.28 | 70.59 | H22 | | 2.82 |
| C5 | - | 50.59 | H23 | 1.36 | 1.01 |
| C6 | 29.34 | 28.96 | H24 | 1.89 | 1.48 |
| C11 | 62.25 | 63.67 | H25 | | 2.29 |
| C14 | 58.51 | 58.55 | H26 | 2.70 | 2.68 |
| C15 | 54.46 | 52.83 | H27 | | 0.69 |
| C16 | 56.51 | 56.89 | H28 | | 2.86 |
| | | | H29 | 3.23 | 3.21 |
| | | | H30 | | 4.19 |
| | | | H31 | | 0.44 |
| | | | H32 | | -0.29 |
| | | | H33 | 3.56 | 3.57 |
| | | | H34 | 3.25 | 3.31 |
| | | | H35 | | 2.61 |
| | | | H36 | | 3.17 |
| | | | H37 | 3.35 | 3.39 |
| | | | H38 | | 2.61 |
| | | | H39 | | 3.17 |

5. Conclusion

The optimized molecular structure, vibrational frequencies and corresponding vibrational assignments of Voglibose have been calculated using B3LYP level with 6-31G(d,p) basis set. Considering that experimental and the theoretical studies are performed in different phase, it can be said that there is a good agreement between the experimental and theoretical data. The reduction of N-H stretching wavenumber is attributed to the N-H...O hydrogen bonding interactions. NBO analysis clearly explains the formation of weak H bonded interaction between the LP(1)N13 and $\pi^*(\text{O}10\text{-H}28)$ antibonding orbitals and charge transfer causing stabilization of energy 4.86 KJmol^{-1} the system. The energies of important MOs and the max of the compound were also evaluated from TD-DFT method. The ^{13}C and ^1H NMR chemical shifts calculated by B3LYP/6-31G(d,p) are closer to the experimental values. Moreover, frontier molecular orbitals and molecular electrostatic potential were visualized. Electronic transition and energy band gap of the title molecule were investigated and interpreted.

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