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An investigation on structural, vibrational and nonlinear optical behavior of 4b,9b-dihydroxy-7,8-dihydro-4bH-Indeno[1,2-b] Benzofuran-9,10(6H,9bH)-dione: A DFT study

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Abstract. A detailed theoretical quantum chemical study on 4b,9b-dihydroxy-7,8-dihydro-4bH-indeno[1,2-b] benzofuran-9,10(6H,9bH)-dione (Dihydroxy-Dihydro-Indeno-Benzofuran-Dione) has been discussed. The structure of the title molecule has been optimized and the structural parameters have been calculated by DFT/B3LYP method with 6-311++G(d,p) basis set. The fundamental vibrational wavenumbers as well as their intensities were calculated and excellent agreement between observed and calculated wavenumbers has been achieved and was interpreted in terms of potential energy distribution analysis. The electronic properties such as HOMO and LUMO energies and associated frontier energy band gap were calculated. Thermodynamical parameters along with the nonlinear optical (NLO) behavior of the title molecule are also discussed. The lower value of frontier orbital energy gap and a higher value of dipole moment suggest that the title compound is highly reactive. The NLO behavior of the title compound has been achieved by dipole moment, polarizability and first static hyperpolarizability. The large value of hyperpolarizability β_{total}, indicates that the title molecule may serve as a good NLO material. The theoretical results were found to be in coherence with the measured experimental data.

Keywords. Benzofuran-dione; FT-IR spectrum; Quantum chemical calculations; DFT; NLO.

1. Introduction

Structural and conformational studies of a molecule give the hypothesis about target ligand interactions whereas synthesis is a route to test this hypothesis by a total synthesis of derivatives.[1,2] The title compound, Dihydroxy-Dihydro-Indeno- Benzofuran-Dione, has been taken from the work of Mehdi *et al.*[3] and is reported to have potential antimicrobial activity comparable to that of clinically used antimicrobial agents against selected microorganisms and selective and moderate inhibitory activity on butyryl cholinesterase enzyme.[3] The present work deals with FT-IR spectroscopic investigation of Dihydroxy-Dihydro-Indeno-Benzofuran-Dione employing the B3LYP method using 6-311++G(d,p) as basis set. In this regard, VEDA 4 program has been used to carry out the potential energy distribution (PED) analysis.[4] Theoretically predicted

values were compared with the experimentally measured data and the results are discussed. A comprehensive investigation was carried out on geometrical and electronic structure of the title molecule such as equilibrium energy, frontier orbital energy gap, molecular electrostatic potential (MESP), dipole moment, polarizability, first static hyperpolarizability for NLO behavior, which may lead to a better understanding of structural and spectral characteristic of the title compound. To the best of our knowledge, neither quantum chemical calculations, nor the vibrational analysis has been reported yet for the title molecule.

2. Experimental

2.1 *Structure*

The crystal structure of the title compound Dihydroxy-Dihydro-Indeno-Benzofuran-Dione is taken from the

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work of Mehdi *et al.*[3] (figure S1 in Supplementary Information (SI)). The molecular structure using numbering scheme of the title compound is given in figure 1 while the structure as seen by Gaussview software is shown in figure 2.

2.2 *Spectroscopic measurements*

The FT-IR spectrum, proton (^{1}H) NMR spectrum and ^{13}C NMR spectrum of the title compound are shown as figures S2, S3 and S4, respectively, in SI, all have been taken from the work of Mehdi *et al.*[3]

3. Result and Discussion

All the calculations were performed on an AMD dual core/2.71 GHz personal computer using Gaussian 03W program package, invoking gradient geometry optimization.[5,6] Figure 1 shows the model molecular structure of the title compound using number scheme for the calculations. Initial geometry was generated from standard geometrical parameters and was minimized without any constraint in the potential energy surface at B3LYP level, adopting the 6-311++G (d, p) basis set. We have utilized the gradient corrected density functional theory (DFT) with the three-parameter hybrid functional (B3) for the exchange part and the Lee–Yang–Parr (LYP) correlation function for the computation of molecular structure, vibrational frequencies, and energies of the optimized structures.[7–9] Vibrational frequencies computed at DFT level have been adjudicated to be more reliable than those obtained by the computationally demanding Moller–Plesset perturbation methods.
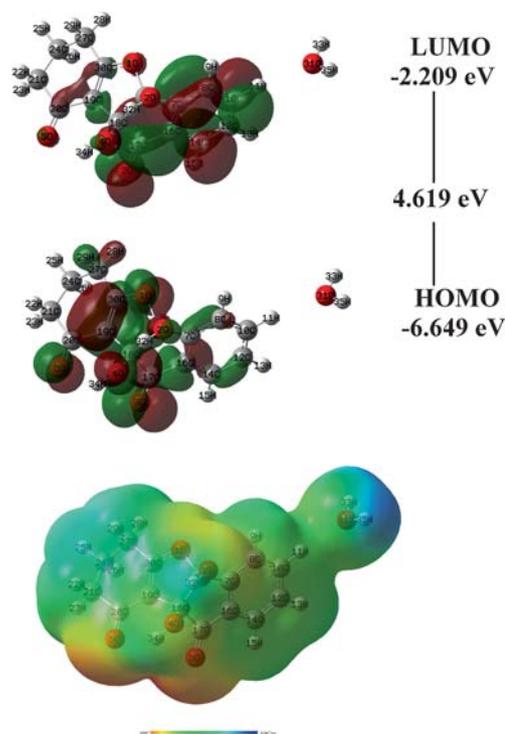
Figure 2. HOMO-LUMO-MESP plot of Dihydroxy-Dihydro-Indeno-Benzofuran-Dione as viewed by the Gaussview 5.0.

DFT offers electron correlation which is frequently comparable to second-order Moller–Plesset theory (MP2).[10,11] The vibrational frequency assignments have been carried out by combining the results of the Gaussview 5.0 program, symmetry considerations and the VEDA 4 program.[12] The optimized structural parameters were then used to calculate the vibrational wavenumbers and the stability of optimized geometry

Figure 1.   Model molecular structure of Dihydroxy-Dihydro-Indeno-Benzofuran-Dione.

was confirmed by the absence of any negative vibrational wavenumbers. To correct overestimations at the calculated harmonic frequencies, an empirical uniform scaling factor of 0.983 up to 1700 cm^{-1} and 0.958 for greater than 1700 cm^{-1} were used.[13,14] The vibrational wavenumber assignments have been carried out using Gaussview 5.0 software. The electronic properties such as HOMO and LUMO energies were also determined to investigate the reactive sites of the compound. 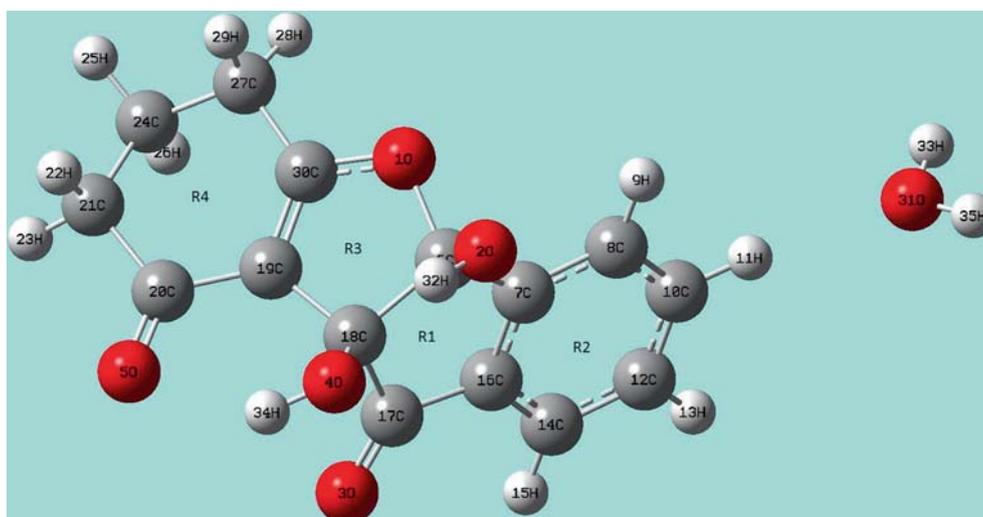The molecular electrostatic potential (MESP) was evaluated using the DFT method. DFT theory has also been used to calculate the dipole moment, mean polarizability $<\alpha>$ and first static hyperpolarizability 'β' based on the finite field approach.[15]

3.1 *Optimized Molecular Geometry*

The molecule under study contains four rings R1-R4, out of these, two rings (R2 and R4) are six member rings and two others (R1 and R3) are five member rings. The equilibrium geometry optimization of lowest energy conformer has been achieved by energy minimization. The calculated vibrational spectrum contains no imaginary wave number which indicates that the optimized geometry of Dihydroxy-Dihydro-Indeno-Benzofuran-Dione molecule is at minima on potential energy surface. All the optimized parameters are shown in table S1 in SI. The optimized bond length of (C-C) in five member ring R1 ranges from 1.4799 to 1.5707 Å. The (C-C) bond length in six member ring R2 is calculated in the range 1.3889–1.4045 Å, whereas it is slightly greater for another six member ring R4 and found in the range 1.4486–1.540 Å. For ring R3 which is a five member ring the optimized bond length for (C1-O1) is calculated as 1.4976 Å, for the (C1-O2) adjacent to ring R1 and R3 is obtained slightly at a lower value as 1.3698 Å, which may be due to attachment of water molecule H1W1-O1W-H2W1. As expected the (C8=O3) adjacent to ring R1 and (C11-O5) adjacent to R4 are found at low values as compared to (C-O) and it is 1.2167 Å and 1.2264 Å, respectively. The bond length (C9-O4) which is outside the ring R3 is greater than the value of (C-O) within the ring and is obtained as 1.4159 Å. The stretching vibrational modes (O-H) like (O2-H102), (O4-H104) and (O1W- H1W1), (O1W-H2W1) are calculated as 0.9714, 0.971, 0.9624 and 0.625 Å, respectively. The optimized bond length of (C-H) such as (C3-H3A), (C4-H4A), (C5-H5A), (C6-H6A), (C12-H12A), (C12-H12B), (C13-H13A), (C13-H13B), (C14-H14A) and (C14-H14B) all are within the range 1.0834–1.0979 Å. Values of all bond angles are given in table S1 in SI and all are in accordance with the reported by others as well as by our previous

work.[16–21] The torsional strain in five member rings R1 and R3 also arises due to the decrease in lateral distance between the bonds on two adjacent carbon atoms. The repulsive interaction between the electrons of the bonds increases which causes a decrease in bond angle. The optimized geometrical parameters represent a good agreement with experimental parameters and are used as the basis for calculating vibrational wavenumbers and thermodynamic parameters.

3.2 *Dipole moment, Polarizability and First static Hyperpolarizability*

Dipole moment, polarizability and hyperpolarizability are important Non-Linear Optical (NLO) response properties for organic molecules. Polarizability and hyperpolarizability can be considered as the quantities related to the first and higher order derivatives of the electron density and are expected to be helpful for investigating the stability of chemical bonds and characteristics of interactions. The density functional theory has also been used to calculate the dipole moment μ, mean polarizability $<\alpha>$ and the total first static hyper polarizability β for the title molecule.[22,23] The calculated value of dipole moment for the title molecule is found to be quite high (7.7818 Debye) and is attributed to the presence of an extra highly electron withdrawing carbonyl group. A greater contribution of α_{YY} in the mean polarizability $<\alpha>$ in the title compound shows that molecule possibly is elongated more towards Y axis and more contracted towards X axis. The total intrinsic hyperpolarizability β_{total} and a component of the first hyper polarizability along the direction of the dipole moment are represented by β. The largest β_{xxx} component of hyperpolarizability β_{total} indicates the charge delocalization along the bond axis and it suggests that the title molecule is relatively more optically active along X axis. The β components of the Gaussian outputs are reported in atomic units, where 1 a.u. = 8.3693 × 10^{-33} e.s.u. The calculated values of μ, $<\alpha>$ and β_{total} for Dihydroxy-Dihydro-Indeno-Benzofuran-Dione, were found to be 7.7818 D, −109.612 a.u (or −0.917 × 10^{-30} e.s.u.) which is nearly five times to that of urea (0.1947 × 10^{-30} e.s.u.) and 447.2694 a.u. (or 3.74 × 10^{-30} e.s.u.), respectively, at B3LYP/6-311++G(d,p) basis set as shown in table 1.

3.3 *Electronic Properties*

The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that largely acts as the electron acceptor. The HOMO and LUMO of a

Table 1. Dipole moment, Polarizability and Hyper Polarizability of the title molecule.

Polarizability Values		Hyper Polarizability Values		Dipole Moment (Debye)	
α_{XX}	−82.6607	β_{XXX}	361.9736	μ	7.7818
α_{XY}	−5.1157	β_{XXY}	143.3747		
α_{YY}	−124.4797	β_{XYY}	42.3298		
α_{YZ}	−5.0927	β_{YYY}	52.7823		
α_{ZZ}	−121.6951	β_{XXZ}	7.5184		
α_{XZ}	−1.8690	β_{XYZ}	11.4230		
$<\alpha>$	−109.612	β_{YYZ}	1.3708		
- -		β_{XZZ}	−2.1811		
- -		β_{YZZ}	−1.1055		
- -		β_{ZZZ}	8.5026		
- -		β_{total}	447.2694		

molecule are referred as frontier orbitals and the gap in energy between these two molecular orbitals is an important stability parameter. These orbitals decide the interaction manner of a molecule with other chemical moieties. Frontier orbital gap with small value tells that molecule is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as a soft molecule.[24,25] According to the present DFT, the plots of the HOMO, LUMO, and electrostatic potential for the title molecule are shown in figure 2.

From 2D plot of HOMO (−6.67 eV), it is clear that most of the negative equipotential (red colour) cloud is spread on ring R4 and the rest of the red portion is associated with atoms O3, O1, O5 O1 and O2 in decreasing order, whereas positive potential cloud (green colour) of HOMO resides mostly on the opposite face of the ring R3 and also some portion on C17 and C18 atoms. This indicates that electrons are transferred from ring R3 to R4 on same side. Charge transfer also seems to occur on atoms C16, C17 and C18 containing both red and green colours. Figure 2 also shows the 2D plot of the LUMOs of the title molecule which suggests that most of the LUMOs are spread over the rings R1 and R2 (−2.209 eV). It is clear that the negative and positive equipotential clouds of LUMOs are on opposite faces of the five member ring R1, phenyl ring R2 and on atom O3 indicating the charge transfer on these moieties from one face to other.

The Molecular Electrostatic Potential (MESP) plot mapped onto the iso-electron density surface, simultaneously displays molecular shape, size and electrostatic potential values in terms of color coding and is a practical tool in the investigation of correlation between molecular structure and the physiochemical property relationship of molecules including biomolecules and drugs.[26–31] The MESP map of the title is also shown at

Table 2. HOMO, LUMO and FO Energy gap for the title molecule.

Parameters	Calculated Values
HOMO (in eV)	−6.6493
LUMO (in eV)	−2.209
Frontier orbital energy gap (in eV)	4.6199

bottom of the figure 2 with color scaling ranging from −0.067 to +0.067 a.u. It is evident from the MESP map that the region around the ring R1 and phenyl ring R2 is electron deficient and have the binding sites for nucleophilic attack. The electron rich regions residing on all the oxygen atoms O1, O1W, O2, O3, and O3W represent the electronegative regions and so, these are the binding sites for electrophilic attack. The values of HOMO, LUMO and Frontier orbital energy gap are given in table 2.

3.4 *Vibrational Assignments*

3.4a *C-H Vibration*: Generally, the aromatic ring vibrational modes are insensitive to the substituent groups while some of the vibrations are substituent sensitive and can provide important structural information due to the mechanical coupling with the substituent group vibrations.[32–34] The asymmetric ν(C-H) stretching vibrations are generally observed in the spectral region 3100–3000 cm^{-1}, while the symmetric stretch appear between 3000–2900 cm^{-1} which is the characteristic region for the ready identification of C-H stretching vibrations.[35] According to the present study for the title compound Dihydroxy-Dihydro-Indeno-Benzofuran-Dione, the C-H asymmetric stretching vibrations are calculated at 3069 and

3065 cm^{-1} and are observed at 3086 and 2970 cm^{-1} in the FTIR spectrum, respectively, with weak absorptions. The symmetric ν(C-H) vibrations are calculated at 3056 and 3046 cm^{-1} and are obtained at frequencies 2960 and 2950 cm^{-1} with weak absorption peaks. All the ν(C-H) modes have very high PED values as shown in table S2 in SI.

3.4b *Methylene (CH$_2$) Group Vibrations*:

The CH$_2$ vibrational modes for the title molecule are calculated at frequencies 2963, 2956, 2947, 2915, 2896 & 2892 cm^{-1}, which are in good agreement with observed frequencies obtained at 2930, 2920, 2915, 2900, 2890 and 2882 cm^{-1}, respectively. All the vibrational modes bear high percentage of potential energy distribution.

3.4c *Carbonyl Absorption (C=O)*:

Carbonyl absorptions are sensitive and both the carbon and oxygen atoms of the carbonyl group move during the vibration and they have nearly equal amplitude. The C=O stretching vibration appears as a prominent mode in FTIR spectrum at 1725 cm^{-1} and 1654 cm^{-1} which are calculated at 1713 and 1654 cm^{-1}, respectively, with 100% and 83% PED, respectively. These two modes are corresponding to antisymmetric and symmetric stretching in C=O, respectively.

3.4d *(C-C) Stretch*:

The ν(C-C) stretching vibrations are observed in FTIR spectrum at frequencies 1458, 1428, 1387, 1367, 1355, 1347 and 1335 cm^{-1} which are calculated at 1438, 1436, 1410, 1401,1373, 1365 and 1334 cm^{-1} respectively. These vibrations are also mixed with in plane bending modes with small PEDs.

3.4e *(C-O) Vibration*:

In the middle of the FTIR spectrum the (C-O) stretching vibration mode are observed at frequencies 1315, 1304, 1280, 1265, 1244, 1223 and 1215 cm^{-1} which are calculated at 1315, 1304, 1289, 1260, 1242, 1227 and 1211 cm^{-1}, respectively. These vibrations are mixed with in plane bending modes of Φ(H-C-C), with low PED values.

3.4f *Some Other Modes*:

In the present study, several torsional modes are observed in the lower-middle portion of the FTIR spectrum. In lower middle region of spectrum, some important torsional modes are obtained at frequencies 928, 898, 878, 867, 862 and 826 cm^{-1}, these are calculated as 924, 883, 873,863, 859, 832 and 817 cm^{-1}, respectively. All these modes have low PEDs and weak absorption except the one at 898 cm^{-1} which

is a very strong peak and it seems to be one of the characteristics absorption peaks of the title molecule. Some other mixed modes are observed at lower part of the FTIR spectrum (800-400 cm^{-1}) with in-plane bending (Φ), out-of-plane bending (ω) and torsional (τ) modes with low PED values and weak absorption peaks. All these mixed vibrational modes are listed in table S2 in SI.

The study of low frequency vibrations is of great significance, because it gives information on weak intermolecular interactions, which takes place in enzyme reactions.[36] Knowledge of low frequency mode is also essential for the interpretation of the effect of electromagnetic radiation on biological systems.[37] In finger print region of FTIR spectrum, due to twist and torsion in the rings, some weak frequency absorption peaks like 456 and 445 cm^{-1} are observed and are calculated at 465 and 436 cm^{-1}, respectively. Some other torsional modes are also calculated at frequencies 218, 88 and 78 cm^{-1} with appreciable intensities. Some discrepancies are observed in the experimental and theoretical intensity in lower range of frequencies, which are due to the impurity of the sample taken, intermolecular interaction, anharmonicity and mixing of different modes of vibrations.

3.4g *Thermodynamic properties*:

The thermodynamical parameters such as the zero-point vibrational energy, the entropy, the heat capacity, rotational constants, enthalpy and dipole moment were computed at B3LYP level using 6- 311++G(d,p) basis set and the results are listed in table S3. The standard statistical thermodynamic functions: heat capacity, entropy and enthalpy changes for the title compound were obtained from the theoretical harmonic wavenumbers in the temperature range 100–700 K. It is observed that these thermodynamic functions increase with increasing temperature due to the fact that the molecular vibrational intensities increase with temperature. The correlation equations between heat capacity (C), entropy (S), enthalpy (H) changes and temperatures (T) are fitted by quadratic formulas. The fitting factors (R^2) for these thermodynamic properties are 0.9988 (for C), 0.9999 (S) and 0.9999 (H), respectively, while the corresponding fitting equations are as follows:

$$C = 3.2509 + 0.1405T - 4 \times 10^{-5}\, T^2 \left(R^2 = 0.9988\right) \tag{1}$$

$$S = 55.19 + 0.1742T - 4 \times 10^{-5}\, T^2 \left(R^2 = 0.9999\right) \tag{2}$$

$$H = -0.2828 + 0.0099T + 6 \times 10^{-5}\, T^2 \left(R^2 = 0.9999\right) \tag{3}$$

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The rotational constants for the title molecule are calculated as 0.55959, 0.18939 and 0.17180 GHz and zero-point vibrational energy as 167.298 kcal/mol.

4. Conclusions

This paper reports a comprehensive theoretical quantum chemical study on 4b, 9b-dihydroxy-7,8-dihydro-4bH-indeno[1,2-b] benzofuran-9, 10(6H,9bH)-dione for the first time. The molecular geometry, vibrational frequency, infrared intensities, NLO behavior and thermodynamical properties of the title molecule have been calculated using DFT (B3LYP) method adopting 6-311++G(d,p) basis set. A good agreement between experimental and calculated normal modes of vibrations is achieved. The lower value of frontier orbital energy gap and a higher value of dipole moment suggest that the title compound is highly reactive. The NLO behavior of the title compound has been achieved by dipole moment, polarizability and first static hyperpolarizability. The large value of hyperpolarizability β_{total}, indicates that the title molecule is a good candidate as a NLO material. The β value is calculated as -0.917×10^{-30} e.s.u, which is nearly five times that of urea. Thermodynamic properties were obtained in the temperature range 100–700 K. In general all the theoretical results show good correspondence with experimental data.

Supplementary Information

All additional information pertaining the crystal structure (figure S1) FTIR spectrum (figure S2) proton NMR spectrum (figure S3), 13C NMR spectrum (figure S4), geometry optimization table (table S1), vibrational assignments (table S2) and thermodynamical properties (table S3) are available in Supplementary Information. Crystallographic data of the title compound has been deposited with the Cambridge Crystallographic Data Center allocated with the deposit number CCDC-824834. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk. CIF file is also given in supplementary files. Supplementary Information is available at www.ias.ac.in/chemsci.

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