ISSN: 2455 – 5428

International Journal of Current Research and Modern Education

Impact Factor 6.725, Special Issue, January - 2017

International Conference on Smart Approaches in Computer Science Research Arena

On 5th January 2017 Organized By

Department of Computer Science, Sri Sarada College for Women (Autonomous), Salem, Tamilnadu

COMPUTATIONAL INVESTIGATION OF N,N'-BIS (2-HYDROXYBENZYLIDENE) –1, 2-DIAMINO BENZENE-MOLECULAR STRUCTURE AND PROPERTIES

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Cite This Article: R. Mathammal, N. Sudha & S. Anbuselvi, "Computational Investigation of N,N'-Bis (2-Hydroxybenzylidene) –1, 2-Diamino Benzene-Molecular Structure And Properties", International Journal of Current Research and Modern Education, Special Issue, January, Page Number 28-30, 2017.

Abstract:

Density functional theory calculations of N, N'-bis(2-hydroxy)benzylidene)-1,2-diaminobenzene with B3LYP/6-311G (d,p) basis set is used to determine ground state molecular geometries, vibrational frequencies, HOMO-LUMO energy gap, Molecular Electro Static Potential surfaces and hyperpolarizibility of 2HBDB.Hyperpolarzibility calculations confirms the Non Linear Optical property of the title compound.

1. Introduction:

The quantum field theory describes the electronic behaviour of atoms and molecules [1,2]. Quantum chemistry mathematically describes the fundamental behaviour of matter at the molecular scale [3]. The ultimate aim of the computational quantum chemistry is to create the efficient mathematical approximation and the computer program calculates the various properties of molecules. The advantage of computational chemistry is to minimize the residual error in the calculation. The computer software being used for quantum chemical calculation in the present work is Gaussian 09 and view the structure through Gauss View 5.0 package.

2. Computational Details:

The molecular structure and physicochemical properties of N, N'-bis(2-hydroxy) benzylidene)-1,2-diaminobenzene(2HBDB) have been studied using DFT calculationswith B3LYP/6-311G(d,p) level of theory [4,5] using Gaussian 09 program.. An empirical uniform scaling factor of 0.956was used to offset the systematic errors caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity. The vibrational frequencies, Dipole moment, Polaraizability, Hyperpolaraizability values, HOMO-LUMO and MESP are determined using Gaussian 09 program.

3. Results and Discussion:

3.1 Optimized Geometry: The optimized molecular structure of 2HBDB which was obtained from Gaussian 09 and Gauss View programs is shown in Fig 1.The positive value of all the calculated wave numbers confirms the stability of optimized geometry. The molecule belongs to C1 point group. The global minimum energy obtained by DFT structure optimization was found to be -1031.4983 Hartees. The bond length of C-C shows 1.4° -1.45°,The C-H bond lengths is in range 1.08°.The C-N bond length is in the range 1.29° -1.295° and O-H has the range 0.9786°.As in the title molecule there are electronegative atoms, bond lengthsare slightly higher than the literature values.

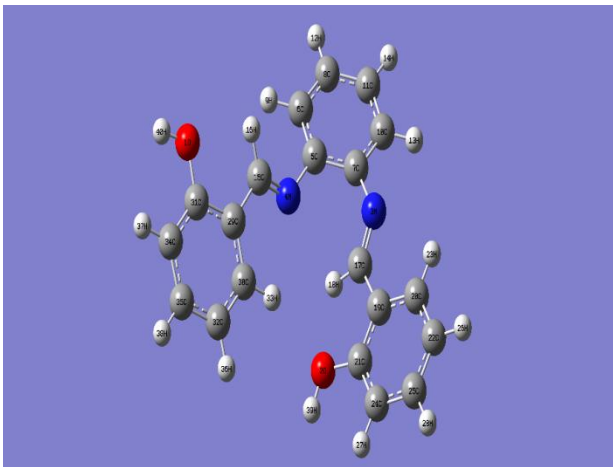

Figure 1: Optimised Structure 2HBDB

3.2 Vibrational Assignments: 2HBDB has 40 atoms 114 modes of vibration and the assignments have been made on Normal Coordinate Vibrational Analysis. It should be noted that the calculations were performed for a free molecule in vaccum and the anharmonicity is neglected in the real systems. The stimulated IR and Raman spectra for 2HBDB is shown in Fig 2 and Fig 3 respectively. The aromatic ring structure shows the presence of C-H stretching vibrations in the region 3100 cm^{-1}-3000 cm^{-1}.In the title compound the corresponding peak is observed at 3100 cm^{-1} in Raman spectra. The ring C-C stretching vibration in the benzene ring is observed at 1500 cm^{-1} in IR .The C=N stretching vibrations is observed at 1600 cm^{-1} .The O-H stretching vibration of 2HBDB is in the region 3650 cm^{-1} -3200 cm^{-1}.In the present study O-H stretching vibrations are stimulated at 3250cm^{-1} and 3600cm^{-1} in IR and 3500 in Raman. The C-O stretching which is generally strong and is observed at 1200cm^{-1} in Raman Spectra.

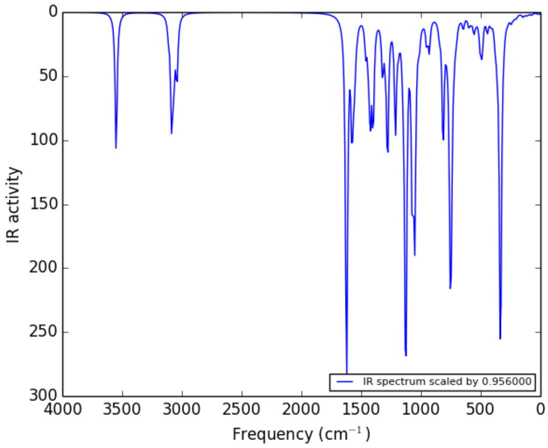

Figure 2: Stimulated IR Spectra of 2HBDB

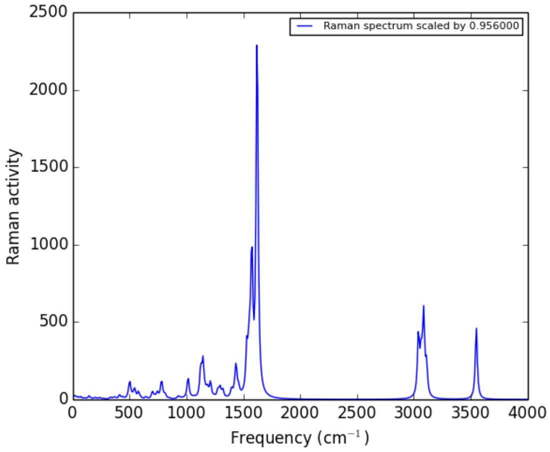

Figure 3: Stimulated Raman Spectra of 2HBDB

3.3 UV-Visible Spectrum: The theoretical UV spectrum generated from optimised structure is performed by DFT method.The maximum absorption at 460 nm shows n→π*transitions of the azomethane group and the spectrum is shown in Fig 4

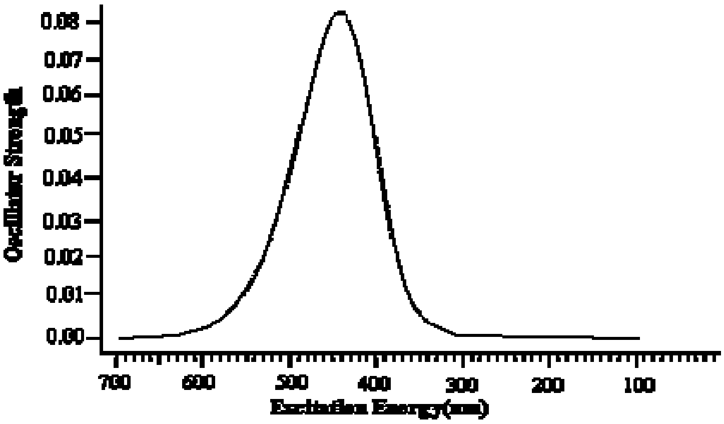

Figure 4: Theoretical UV Spectrum

3.4 Frontier Molecular Orbital Analysis: The study of frontier molecular orbitals; highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO),are the promising method to realise the molecular interaction. The HOMO and LUMO act as an electron donor and electron acceptor respectively. Therefore, the energy of HOMO is directly related to ionization potential and energy of LUMO is directly related to electron affinity. The eigenvalue of HOMO and LUMO and their energy gap reflect the chemical activity of the molecule.

HOMO Energy= -0.1906 kcal/mol
LUMO Energy= -0.05920 kcal/mol
Energy Gap ΔE =-0.13335 kcal/mol

The energy difference between HOMO & LUMO orbital is called as energy gap. It is a critical parameter [6] in determining molecular electrical transport properties.

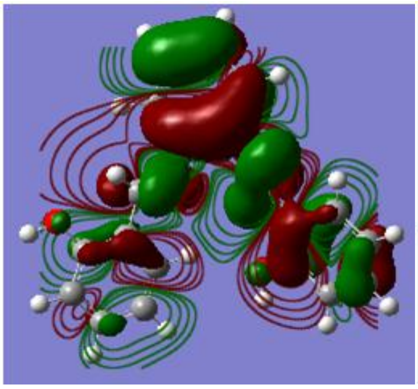

Figure 5: HOMO

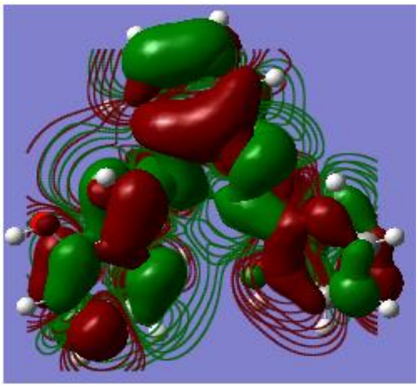

Figure 6: LUMO

3.5 Molecular Electrostatic Potential: MESP provides a visual method to understand the relative polarity of the molecule. The MESP is a plot of electrostatic potential mapped on the constant electron density surface and simultaneously displays molecular size and shape and electrostatic potential values in terms of color grading which is shown in Fig 7. The MESP map in case of 2HBDB clearly suggests that the potential swings wildly between oxygen atoms (dark red) and benzene ring (blue). The oxygen atoms of hydroxy group (reflects the electronegative region) show high nucleophilic activity due to excess negative charges and the hydrogen atoms attached to the benzene ring bear most of positive charge (blue region) and may be centre for electrophilicity activity. From this result, we can say that the H atoms indicate the strongest attraction and O atoms indicates the strongest repulsion.

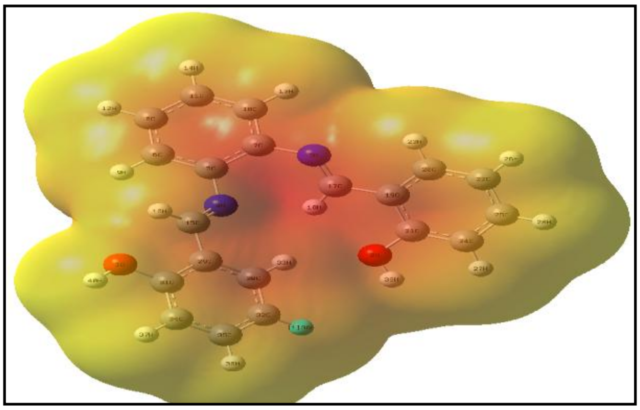

Figure 7: MESP plot of 2HBDB

3.6 NLO Properties: The hyperpolarizability, a nonlinear-optical property of a molecule, is the second-order electric susceptibility per unit volume. The potential application of the title molecule in the field of nonlinear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes using IR and Raman spectroscopy. Urea is the prototypical molecule used in the study of NLO property of the molecular system. Therefore, urea was used frequently as a threshold value for comparative purposes. In this study, the calculated β value is nearly 19 times that of urea. The large β value calculated shows that the studied compound is a good NLO material[7,8].

Table 1: Theoretical polarizability data of HBDB

	α_{xx} (a.u)	α_{xy} (a.u)	α_{yy} (a.u)	α_{xz} (a.u)	α_{yz} (a.u)	α_{zz} (a.u)	α_{tot} (e.s.u)	$\Delta\alpha$ (e.s.u)
HBDB	305.7481	-0.0089	221.4185	0.0155	2.2757	217.769	3.6800 x10^{-23}	1.2790 x10^{-23}

Table 2: Theoretical hyperpolarizability data of HBDB

	β_{xxx} (a.u)	β_{yxx} (a.u)	β_{xy} (a.u)	β_{yyy} (a.u)	β_{zxx}(a.u)	β_{zyy} (a.u)	β_{xzz} (a.u)	β_{yzz} (a.u)	β_{zzz} (e.s.u)	β_{tot} (a.u)
2HBDB	0.5066	-531.4971	0.1913	-172.3321	253.4073	109.7682	0.04580	122.7675	226.8780	7.1544 x10^{-30}

4. Conclusion:

The DFT calculations were carried out to study the structural,opto-electronic properties of 2HBDB using Gaussian 09 program. The structure has been optimised at B3LYP/6-311G(d,p) level of theory. The peak absorbed at 460 nm shows that the molecule is highly conjugative. The IR and Raman spectrum confirms the presence of functional groups. The value low of ΔE of the compound shows it can be used for NLO activity. The large β value calculated shows that the compound is a good NLO material and can be used for Opto-Electronic Industries

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