

CHARGE TRANSFER INTERACTION AND SPECTROSCOPIC STUDIES ON 5-ETHYL-2-HYDROXY BENZALDEHYDE NLO MATERIAL

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Abstract-Quantum chemical calculations of energies, geometrical structure and vibrational wavenumbers of 5-ethyl-2-hydroxy benzaldehyde have been calculated by employing MP2 level of theory using the 6-31G(d) basis set. Fourier transform IR spectral study has been performed to identify the functional groups. 5-ethyl-2-hydroxy benzaldehyde is used in electro-optic switching elements for telecommunication, optical information processing, optical parametric oscillator and degenerate four wave mixing because of its NLO activity. Spectroscopic analysis has been performed using experimental methods. The electric dipole moment (α) and the first hyperpolarizability (β) values of the investigated molecule have been computed using MP2 calculations. NBO analysis has been performed to study the charge transfer interaction. The calculated results also show the nonlinear optical (NLO) behaviour of the title compound. The UV-Vis spectrum confirmed the transparency of the compound between the wavelengths 200 and 700 nm. The NLO property of 5-ethyl-2-hydroxy benzaldehyde was confirmed from the second-harmonic generation by Kurtz-Perry powder test.

I. Introduction

Nonlinear optical materials have recently been employed in a variety of technological applications, such as optical communications, computation, optical switching and limiting and dynamic image processing, due to their ability to alter the properties of applied electromagnetic fields uniquely, especially in frequency and phase [1, 2]. They are promising systems for other optical applications also such as holographic and digital storage, liquid crystal command surfaces, and nonlinear optical devices [3, 4]. Most molecular nonlinear optical materials, however, are relatively inefficient photonic modulators. 5-ethyl-2-hydroxy benzaldehyde is the potential organic nonlinear optical material. Second harmonic generation (SHG) efficiency of crystalline materials depends both on the magnitude of molecular hyper polarizability (β) and on the orientation of the molecules. The 5-ethyl-2-hydroxy benzaldehyde exhibits good non-linear optical property. 5-ethyl-2-hydroxy benzaldehyde is trisubstituted benzene with -CHO, -OH and -C₂H₅ groups substituted the ring. This sample is a donor-acceptor substituted benzene derivative.

II. EXPERIMENTAL DETAILS

The FT-IR spectrum of the compound 5-ethyl-2-hydroxy benzaldehyde was recorded in the range of 4000-400 cm⁻¹. The ¹H and ¹³C NMR spectra were recorded (in CDCl₃) on Bruker AVANE III 500 MHz (AV500) NMR spectrometer at 300 MHz for ¹H and 75 MHz for ¹³C NMR using tetramethylsilane (TMS) as an internal standard. The second harmonic generation behaviour of the powdered material was tested using the Kurtz and Perry method.

III. COMPUTATIONAL DETAILS

The entire calculation was performed at MP2-B3LYP/6-31G (d) basis set using the Gaussian 09W program. The vibrational frequencies, Infrared intensities of the title molecule are calculated. The natural bonding orbital (NBO) calculation were performed using NBO3.1 program as implemented in Gaussian 09W[5] package at MP2/B3LYP/6-31G(d) level in order to understand interactions between the another subsystem, which is a measure of the intramolecular delocalization or hyper-conjugation [6].

IV. RESULTS AND DISCUSSION

The optimized molecular geometry of the sample (Fig:1) was calculated using Gaussian'09W program. The phenyl ring appears a little deviated with C₃-C₅, C₃-C₆, and C₄-C₇ and C₇-C₈ bond lengths due to the substitution. These deviations are explained in terms of the change in hybridization due to the substituent at the carbon to which it is attached. C₄-C₁₀ bond length value is (1.481). The angles are also slightly deviated from the standard value 120° which the substitution of electronegative oxygen atom and the aldehyde group in place of hydrogen atoms.

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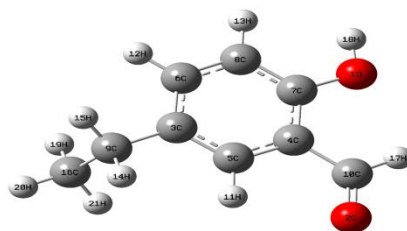


Fig: 1 Optimized structure of 5-ethyl-2-hydroxy benzaldehyde MP2/6-31G(d) basis set.

Table 1: Selected optimized parameters of 5-ethyl-2-hydroxy benzaldehyde,

Bond length	Experimental value (Å)	calculated value (Å)	Bond angle	Experimental value (°)	calculated value (°)
O ₁ -C ₇	1.349	1.374	C ₃ -C ₅ -C ₄	121.9	121.7
O ₂ -C ₁₀	1.206	1.230	C ₅ -C ₃ -C ₆	117.2	117.9
C ₃ -C ₅	1.385	1.395	C ₅ -C ₄ -C ₇	119.5	119.2
C ₃ -C ₆	1.383	1.403	C ₃ -C ₆ -C ₈	123.2	121.3
C ₄ -C ₅	1.402	1.400	C ₆ -C ₃ -C ₉	121.5	120.8
C ₄ -C ₇	1.390	1.404	O ₁ -C ₇ -C ₄	119.5	117.7
C ₄ -C ₁₀	1.471	1.481	O ₁ -C ₇ -C ₈	120.7	122.5
O ₁ -H ₁₈	0.820	0.973	C ₅ -C ₄ -C ₁₀	119.1	119.2

Vibrational analysis

The title molecule consists of 21 atoms and so they have 57 normal vibrational modes. The experimental FT-IR spectrum of title molecule is shown in Fig.2. The fundamental vibrational wavenumbers of the compound calculated by MP2 and B3LYP/6-31G(d) methods. The normal modes of vibration were assigned on the basis of TED.

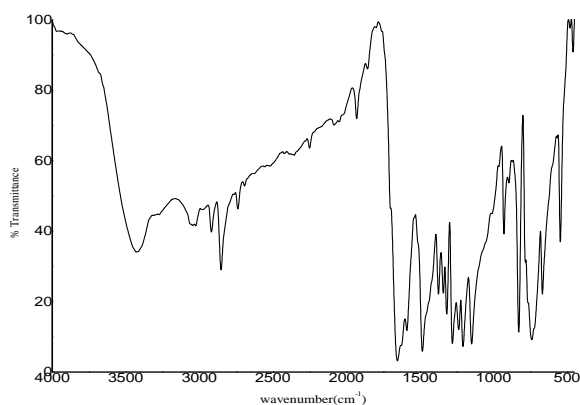


Fig.2.FT-IR Spectrum of 5-ethyl-2-hydroxy benzaldehyde,

Hydroxyl and CO vibrations

The O-H group gives rise to three vibrations such as stretching, inplane bending and out-of-plane bending vibrations. The hydroxyl stretching vibrations are generally observed in the region around 3500 cm⁻¹. In this molecular spectrum, a strong broad absorption observed at 3427 cm⁻¹ (IR) is assigned to O-H stretching vibration. The stretching vibrational wavenumber of O-H region is unchanged, means the bound O-H is red shifted. The red

shift of the O-H stretching wave number is due to the formation of strong O-H...O hydrogen bonds by hyperconjugation between aldehyde oxygen lone electron pairs and σ^* O-H anti bonding orbitals.

Ring vibrations

The ring carbon-carbon stretching vibrations occur in the region 1430–1625 cm^{-1} . In benzene ring the bands are of variable intensity and are observed at 1625–1280 cm^{-1} from the frequency ranges given by Varsanyi [7]. In the present work, the frequencies observed in FT-IR spectrum at 1590 and 1321 cm^{-1} . The theoretically computed values of are identified at 1630 and 1644 cm^{-1} . The bands 3045, 3024 cm^{-1} are assigned to C-H stretching vibrations in FT-IR wave numbers. The C-H in-plane bending vibrations are assigned to the very strong bands at 1237, 1136 cm^{-1} and the medium bands at 953, 820 cm^{-1} are assigned to C-H out-of-plane bending vibration in FT-IR [8, 9].

C-CHO vibrations

The C-CHO stretching vibration for aldehyde gives rise to band in the range 1230–1160 cm^{-1} [10]. The recorded spectrum shows very strong band in FT-IR attributed to C-CHO stretching vibration. The strong intense band is obtained at 155 cm^{-1} in FT-IR is assigned to the in-plane vibration of C-CHO. The out-of-plane bending vibration is attributed to 243 cm^{-1} in FT-IR spectrum. The aldehydic C-H stretching wavenumber occurs lower than the most other C-H stretching vibrations. The presence of band at about 2921 cm^{-1} is assigned to C-H stretching in aldehyde and a band due to the carbonyl stretching vibration in the region 1765–1685 cm^{-1} may usually be taken as indicating the presence of an aldehyde.

NBO Analysis

NBO method is that it gives information about interactions in both filled and unfilled spaces that could enhance the analysis of intra- and intermolecular interactions. The second order Fock matrix was evaluate the donor-acceptor interactions in the NBO analysis [11]. Natural bond orbital analysis a logical method for learning intra and intermolecular bonding and interaction among bonds, and also provides a suitable basis for charge transfer or conjugative interaction in molecular systems. The larger the $E^{(2)}$ value denote the more intensive is the interaction between electron donors and electron acceptors. The stabilization energy contributions from the σ ($\text{C}_3\text{-C}_5$) \rightarrow σ^* ($\text{C}_4\text{-C}_{10}$) interactions is 11.84 kJ/mol and σ ($\text{C}_4\text{-C}_7$) \rightarrow σ^* ($\text{C}_7\text{-C}_8$) interactions is 17.6 kJ/mol.

Charge analysis

Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. It is used to represent the charge movement across the molecule. The dipole moment vector depends on only the centers of positive and negative charges in a molecule. Natural charge calculation has a main role in the molecular system because it is used to explain the atomic charges effect, dipole moment, molecular polarizability, electronic structure and more a lot of properties of molecular system. The Natural charges at the sites of the atom C_{10} is more positive (0.413e) and C_7 is positive (0.366e) charge which suggests an extensive charge delocalization in the entire molecule through $\text{C}_4\text{-C}_{10}$ and $\text{C}_4\text{-C}_7$. The shortening of the $\text{C}_4\text{-C}_{10}$ and $\text{C}_4\text{-C}_7$ bonds also supports this result. The more negative values on C_3 atom of C_2H_5 group leads to a redistribution of electron density. The H_{18} atom attached with highly electronegative oxygen atom making that hydrogen more electron deficient, so that it occurs more positive charge. The negative charges located at atoms O_1 and O_2 will interact with C_7 and C_{10} atoms due to inductive effect, the bond distance $\text{C}_4\text{-C}_{10}$ (1.481 Å) increases. The charge analysis shows that the presence of C_{10} imposes highly positive charge on the oxygen atom of the aldehyde group. Ethyl hydrogen is more positive than ring hydrogen atoms. The largest positive charge occurs at H_{18} , which are involved in weak C-H...O hydrogen bonding with Natural charges.

Potential energy surface scan study

The possible conformations of 5-ethyl-2-hydroxy benzaldehyde potential energy scans were performed for the dihedral angle D ($\text{O}_1\text{-C}_7\text{-C}_8\text{-H}_{18}$) at the MP2/6-31G (d) level of theory. The scans were obtained by the potential energy in all geometrical parameters by varying the torsion angles at a step of 10° in the range of 0–360° rotation around the bond. For this rotation potential energy curve has been shown in fig. The geometry is confined to its local minimum as a consequence of imposing symmetry constraints while optimizing geometry. The steric effect is due to weak van-der Waals repulsive interaction between the positively charge (OH) hydrogen and aldehyde group hydrogen atoms. Clearly demonstrates that corresponds to the global minimum energy -1208341.7KJ/mol. The maximum energy obtained at 90° and 270° corresponds to the global maximum energy -1405915.8KJ/mol. In this compound $\text{H}_{13}\text{-H}_{18}$ distance minimum occurred in 2.292 at an angle 0° and maximum distance occurred in 2.740 at an angle 90°.

Table 2: Potential energy surface scan value of 5-ethyl-2-hydroxy benzaldehyde.

Potential energy surface scan					
Angle (°)	Energy (KJmol ⁻¹)	Distance (Å)			
		C ₇ -C ₈	C ₇ -O ₁	C ₄ -C ₇	H ₁₃ -H ₁₈
0	-1405934.246	1.3849	1.3625	1.4156	2.292
90	-1405915.868	1.3792	1.3863	1.4148	2.740
180	-1405926.37	1.3843	1.3662	1.4233	3.499
270	-1405915.868	1.3792	1.3864	1.4148	2.740
360	-1405936.872	1.3850	1.3619	1.4158	2.279

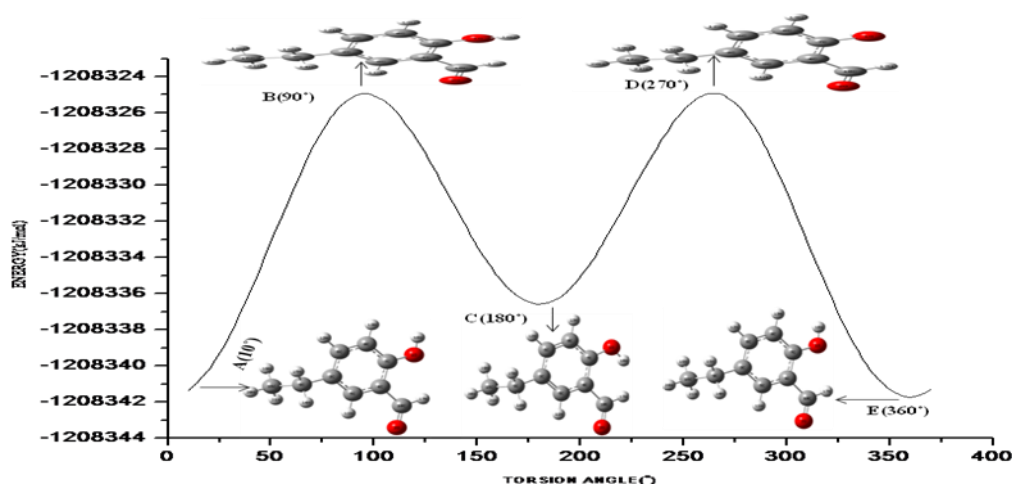


Fig: 3 Potential energy surface scan plot of 5-ethyl-2-hydroxy benzaldehyde,

Homo lumo energy

HOMO and LUMO are acronyms for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively. The energy difference between the homo and lumo is termed the HOMO–LUMO gap. HOMO, means the outermost orbital containing electrons, tends to give these electrons such as an electron donor. LUMO means the innermost orbital containing vacancies to accept electrons. The interaction between HOMO and LUMO orbital of a molecular structure, transition state, transition of π – π^* type is observed with the molecular orbital theory. In this molecule the HOMO–LUMO energy gap value is $= 0.33764\text{eV}$. The energy gap HOMO-LUMO explains the charge transfer interaction with in the molecules.

Non-linear optical (nlo) properties

The first order hyperpolarizability α and β values of Gaussian09W output are in atomic units (a.u.) so they have been converted into electronic units (e.s.u.) (a; $1 \text{ a.u.} = 0.1482 \times 10^{-24} \text{ e.s.u.}$, b; $1 \text{ a.u.} = 8.6393 \times 10^{-33} \text{ e.s.u.}$). The calculated first hyperpolarizability of the title molecule is comparable with the reported values of other NLO molecules, but experimental evaluation of this data is not readily available. Urea is one of the first NLO molecules and the values of its NLO properties are used frequently as a threshold for relative purposes. The value of hyperpolarizability of the sample 5-ethyl-2-hydroxy benzaldehyde $1.7454 \times 10^{-30} \text{ esu}$. The value of hyperpolarizability of the title sample is 4.6807 times greater than urea. All these results are indicating the application as NLO material.

V. CONCLUSION

In the present work the complete molecular structural analysis and vibrational frequencies of the fundamental modes of samples has been determined using MP2 calculations using 6-31G (d) basis is set. The detailed interpretation of the normal modes has been made on the basis of PED calculations. The computed

optimized parameters are in good agreement with those obtained by experimental data. C₄-C₁₀ bond length is deviated (1.481). This bond length is due to the aldehyde group. The first order hyperpolarizability of the title compound is 4.6807 times greater than urea which shows the nonlinear optical activity.

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