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Experimental and Theoretical (ab initio and DFT) Analysis of UV-Vis Spectra, Thermodynamic Functions and Non-linear Optical Properties of 2-Chloro-3,4-Dimethoxybenzaldehyde

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ABSTRACT

In the present work, UV- Visible spectra of 2-Chloro-3,4-Dimethoxybenzaldehyde (2,3,4-CDMB) compound have been carried out experimentally and theoretically. The ultraviolet absorption spectrum of title compound in three solvents (Acetone, Diethyl Ether, CCl_4) of different polarity were examined in the range of 200–500 nm. The structure of the molecule was optimized and the structural characteristics were determined by HF and DFT (B3LYP) methods with 6-31+G(d,p) and 6-311++G(d,p) as basis sets. The excitation energy, wavelength corresponds to absorption maxima (λ_{max}) and oscillator strength (*f*) are calculated by Time-Dependent Density Functional Theory (TD-DFT) using B3LYP/6-31+G(d,p) and B3LYP/6-311++G(d,p) as basis sets. The electric dipole moment (μ), polarizability (α) and the first hyperpolarizability (β) have been computed to evaluate the non-linear optical (NLO) response of the investigated compound by HF and DFT (B3LYP) with already mentioned basis sets. Thermodynamic functions of the title compound at different temperatures were also calculated.

Keywords

2,3,4-CDMB, UV-Visible spectra, HF, DFT, B3LYP, polarizability, the first hyperpolarizability, NLO properties.

Academic Discipline And Sub-Disciplines

Science (Physics)

SUBJECT CLASSIFICATION

Physics (Molecular Spectroscopy)

TYPE (METHOD/APPROACH)

Quasi-Experimental;

1. INTRODUCTION

The benzaldehyde and its derivatives have received attention because of their chemical and biological importance [1-5]. Benzaldehyde is the simplest representative of the aromatic aldehydes. It is found in cherries, almonds, apricot and peach pits. Benzaldehyde is best known as being artificial essential oil of almond and it has many other uses such as; the manufacturing of dyes, perfumes, flavorings, cinnamic and mandelic acids, and it is also used as a solvent. Some more recent developments in the use of benzaldehyde are for the health and agriculture industries. Benzaldehyde is being used as a pesticide and also as an anticancer agent. It is used as a bee repellant in the harvesting of honey. These uses are still in development but would be very helpful in solving some of these problems of today. The benzaldehyde and substituted benzaldehydes have been subjected to various spectroscopic studies [6–14]. Mono-, halo-, methoxy and ethoxy-substituted benzaldehydes, among others, have attracted the attention of the spectroscopists. Various spectroscopic studies of halogen and methyl substituted compounds have been reported in the literature from time to time. N.Sundaraganesan et al., [11] have studied the vibrational spectra of 3,4-dimethylbenzaldehyde. V.Krishnakumar and V.Balachandran have reported vibrational spectra of 2-hydroxy-3-methoxy-5-nitrobenzaldehyde [12]. H Ünver , et.al, [13] have studied the UV-vis spectra and NLO properties of 2-hydroxy-3-methoxy-*N*-(2-chloro-benzyl)-benzaldehyde-imine. V. Venkataramanan, et.al, [14] have studied NLO properties of 3- methoxy–4–hydorxy benzaldehyde. Likewise, several UV-Vis spectroscopic studies, NLO properties, thermodynamic functions on di- and tri-substituted benzaldehydes have been reported [15 -17].

It is observed that the electronic data, non-linear optical parameters and thermodynamic parameters at various temperatures, which are vital to elucidate the relations among energetic, structural and reactivity of the title molecule, are insufficient in the literature. Thus, an attempt has been made in the present work to compute and compare the ground state optimized molecular geometrical parameters, thermodynamic and electronic properties using the Hartree–Fock (HF) and Becke's three parameter exact exchange functional (B3) combined with gradient corrected correlation functional of Lee, Yang and Parr (LYP) methods with 6-31+G(d,p) and 6-311++G(d,p) basis sets.

The UV spectrum was measured in different solvents (Acetone, Diethyl Ether and Carbon Tetra Chloride). The excitation energy, wavelength corresponds to absorption maxima (λ_{max}) and oscillator strength are calculated by Time-Dependent Density Functional Theory (TD-DFT) using B3LYP/6-31+G(d,p) and B3LYP/6-311++G(d,p) as basis sets. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. The non-linear optical parameters (the electric dipole moment, polarizability and the first hyperpolarizability values) of the investigated compound were also calculated using HF (Hartree-Fock) and DFT methods with same basis sets. The experimental and theoretical values of thermodynamic parameters at different temperatures are also tabulated.

2. EXPERIMENTAL DETAILS

The compound under investigation namely 2,3,4-CDMB in the solid form was purchased from Sigma–Aldrich Chemical Pvt. Ltd., Germany with a stated purity of 99% and it was used as such without further purification. The UV/Vis Absorption spectrum of 2,3,4-CDMB was examined in the range 200-500 nm using Perkin Elmer Lambda -25 UV/Vis spectrometer at IIT Roorkee.

3. COMPUTATIONAL DETAILS

The first task for the computational work was to determine the optimized geometry of the title compound that was done by Gaussian 09 program. The HF and DFT (hybrid B3LYP: the Becke's three-parameter hybrid method with the Lee, Yang and Parr correlation functional) [18,19] method with 6-31+G(d,p) and 6-311++G(d,p) basis sets was chosen for compound 2,3,4-CDMB. The entire calculations were performed by using the Gaussian 09 program package on a personal computer [20]. The electronic absorption spectra for optimized molecule calculated with the time dependent density functional theory (TD-DFT) at B3LYP/6-31+G(d,p) and B3LYP/6-311++G(d,p) levels. The time-dependent HF and DFT (TD-HF and TD-DFT) proved to be a powerful and effective computational tool for the study of ground and excited state properties by comparison to the available experimental data. Hence, we used TD-B3LYP to obtain excitation energy, wavelengths (λ_{max}), oscillator strengths and compare with the experimental UV–vis absorption spectra of 2,3,4-CDMB. The non linear parameters (dipole moment, polarizability and first order hyperpolarizability) also calculated by using HF and DFT methods with the same basis sets.

4. RESULT AND DISCUSSION

4.1 Molecular Geometry

The optimized structure parameters of 2,3,4-CDMB calculated by HF and DFT-B3LYP levels with the basis sets 6-31+G(d,p) and 6-311++G(d,p) are listed in Table 1, in accordance with the atom numbering scheme given in Fig.1. Since the crystal structure of the title compound is not available till now, the optimized structure can be only be compared with other similar systems for which the crystal structures have been solved [21, 22]. For example, the optimized bond lengths of C–C in phenyl ring fall in the range from 1.375 to 1.399 Å for HF and 1.38 to 1.48 Å. The bond angles calculated using various methods show the same trends as significant variation in bond lengths. The C-C-C angle in the ring at the position of chlorine substitution is distinctly larger than the others. The remaining C-C-C angles are close to 120^0. The HF and DFT calculations also give shortening of the angle C3–C2–Cl12 for 2,3,4-CHMB and increase of the angle C1–C2–C3 for 2,3,4-CDMB from normal 120^0 at the C2 position and similarly for 3,4,5-CDMB shortening of the angle C4–C3–Cl12 and increase of the angle C2–C3–C4 for from normal 120^0 at the C3 position, and this asymmetry of exocyclic angles reveals the repulsion between the Cl group and the phenyl ring. Based on above comparison, although there are some differences between our values and the literature data, the optimized structural parameters can well reproduce the literature ones and they are the bases for thereafter discussion. The C–Cl bond length is almost equal in all B3LYP basis sets. The C–Cl bond length indicates a considerable increase when substituted in place of C–H. This has been observed even in benzene derivatives [22].

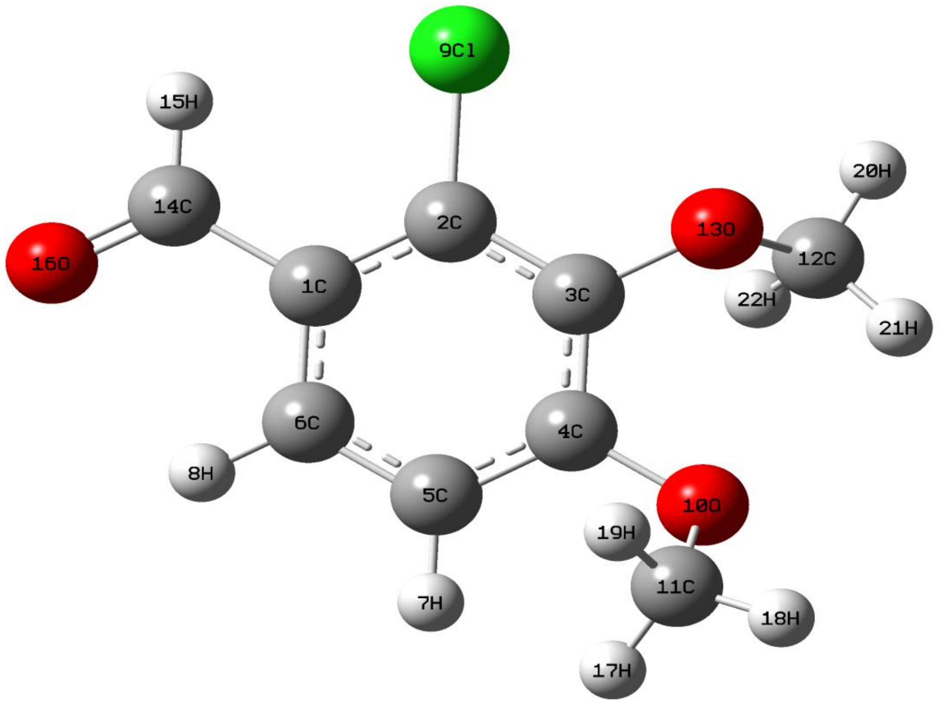


Fig. 1: **The optimized geometric structure with atoms numbering of 2,3,4-CDMB.**

Table 1: Optimized geometrical parameters bond lengths (Å), bond angles (^{0}), and dihedral angles (Å) of 2,3,4-CDMB.

Parameters	6-31+G(d,P)		6-311++G(d,P)	
	HF	B3LYP	HF	B3LYP
Bond Length (Å)				
C1-C2	1.400	1.413	1.398	1.409
C1-C6	1.390	1.405	1.387	1.402
C1-C14	1.489	1.484	1.490	1.484
C2-C3	1.392	1.404	1.390	1.400
C2-Cl9	1.732	1.742	1.733	1.742
C3-C4	1.402	1.413	1.401	1.410
C3-O13	1.352	1.369	1.350	1.366
C4-C5	1.384	1.397	1.382	1.393
C4-O10	1.346	1.367	1.344	1.364
C5-C6	1.379	1.389	1.377	1.385
C5-H7	1.074	1.085	1.073	1.083
C6-H8	1.076	1.087	1.076	1.085
O10-C11	1.411	1.441	1.410	1.440
C11-H17	1.080	1.091	1.081	1.089
C11-H18	1.080	1.096	1.080	1.094
C11-H19	1.085	1.092	1.086	1.090
C12-O13	1.416	1.440	1.415	1.439

C12-H20	1.080	1.091	1.081	1.089
C12-H21	1.080	1.095	1.080	1.093
C12-H22	1.084	1.095	1.085	1.094
C14-H15	1.095	1.112	1.096	1.112
C14-O16	1.188	1.215	1.182	1.208
Bond Angle (^{0})				
C2-C1-C6	118.2	118.1	118.1	118.1
C2-C1-C14	126.1	126.0	126.2	126.0
C1-C2-C3	121.0	120.6	121.1	120.7
C1-C2-Cl9	121.0	122.0	121.0	121.9
C6-C1-O14	115.7	115.9	115.7	115.9
C1-C6-C5	121.6	122.0	121.6	122.0
C1-C6-H8	119.1	118.3	119.0	118.3
C1-C14-H15	112.4	112.3	112.1	112.0
C1-C14-O16	127.7	127.7	127.9	127.8
C3-C2-Cl9	117.9	117.4	117.9	117.4
C2-C3-C4	119.2	119.6	119.1	119.5
C2-C3-O13	122.0	120.9	122.0	121.1
C4-C3-O13	118.6	119.4	118.7	119.3
C3-C4-C5	120.0	120.1	120.0	120.1
C3-C4-O10	123.0	121.1	122.9	121.0
C3-O13-C12	118.2	114.9	118.0	115.0
C5-C4-O10	116.8	118.7	116.9	118.8
C4-C5-C6	119.9	119.5	120.0	119.5
C4-C5-H7	118.5	118.8	118.5	118.7
C4-O10-C11	121.3	116.7	121.1	116.6
C6-C5-H7	121.5	121.7	121.5	121.7
C5-C6-H8	119.3	119.7	119.4	119.7
O10-C11-H17	105.9	105.6	106.1	105.7
O10-C11-H18	111.1	109.9	111.2	109.9
O10-C11-H19	110.8	111.2	110.8	111.2
H17-C11-H18	109.6	109.5	109.4	109.5
H17-C11-H19	109.1	110.3	109.0	110.2
H18-C11-H19	110.3	110.2	110.2	110.2
O13-C12-H20	106.0	105.9	106.1	106.0
O13-C12-H21	111.5	110.6	111.5	110.6
O13-C12-H22	110.8	110.6	110.9	110.6
H20-C12-H21	109.5	109.5	109.4	109.5
H20-C12-H22	109.6	109.9	109.5	109.9
H21-C12-H22	109.5	110.2	109.4	110.2
H15-C14-H16	119.9	120.0	120.0	120.2
Dihedral Angle (Å)				

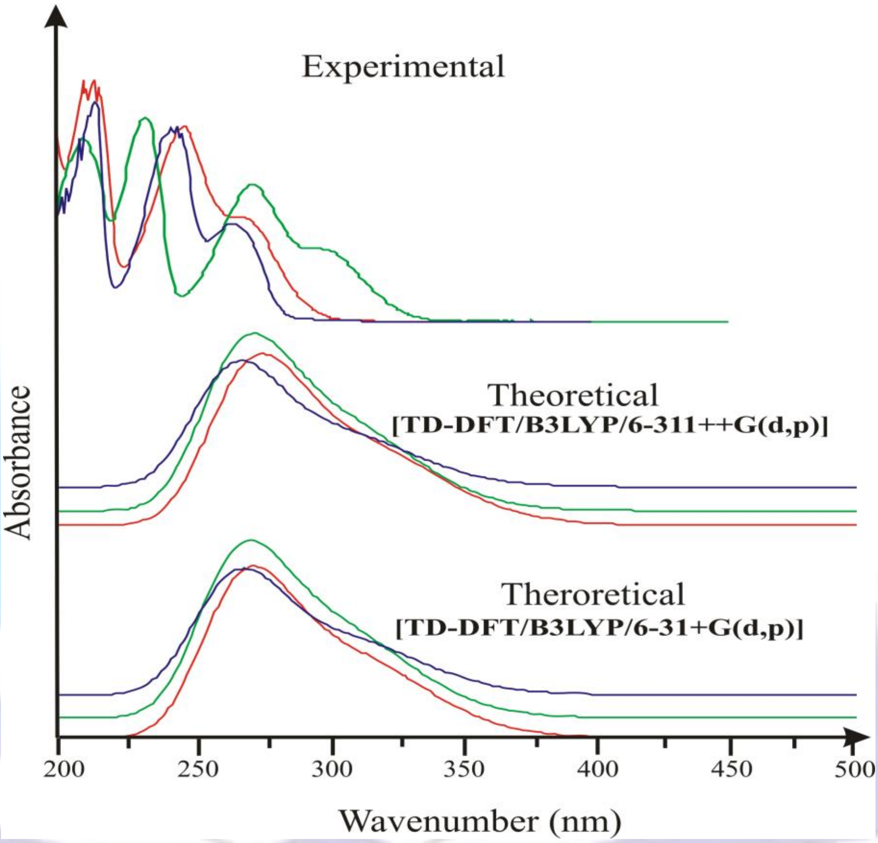
C6-C1-C2-C3	0.0	0.0	0.0	0.0
C6-C1-C2-Cl9	180.0	180.0	180.0	180.0
C14-C1-C2-C3	180.0	180.0	180.0	180.0
C14-C1-C2-Cl9	0.0	0.0	0.0	0.0
C2-C1-C6-C5	0.0	0.0	0.0	0.0
C2-C1-C6-H8	180.0	180.0	180.0	180.0
C14-C1-C6-C5	180.0	180.0	180.0	180.0
C14-C1-C6-H8	0.0	0.0	0.0	0.0
C2-C1-C14-H15	0.0	0.0	0.0	0.0
C2-C1-C14-O16	180.0	180.0	180.0	180.0
C6-C1-C14-H15	180.0	180.0	180.0	180.0
C6-C1-C14-O16	0.0	0.0	0.0	0.0
C1-C2-C3-C4	0.0	0.0	0.0	0.0
C1-C2-C3-O13	180.0	180.0	180.0	180.0
Cl9-C2-C3-C4	180.0	180.0	180.0	180.0
Cl9-C2-C3-C13	0.0	0.0	0.0	0.0
C2-C3-C4-C5	0.0	0.0	0.0	0.0
C2-C3-C4-O10	180.0	180.0	180.0	180.0
O13-C3-C4-C5	180.0	180.0	180.0	180.0
O13-C3-C4-O10	0.0	0.0	0.0	0.0
C2-C3-O13-C12	180.0	180.0	180.0	180.0
C4-C3-O13-C12	0.0	0.0	0.0	0.0
C3-C4-C5-C6	0.0	0.0	0.0	0.0
C3-C4-C5-H7	180.0	180.0	180.0	180.0
O10-C4-C5-C6	180.0	180.0	180.0	180.0
O10-C4-C5-H7	180.0	180.0	180.0	180.0
C3-C4-O10-C11	0.0	0.0	0.0	0.0
C5-C4-O10-C11	0.0	0.0	0.0	0.0
C4-C5-C6-C1	180.0	180.0	180.0	180.0
C4-C5-C6-H8	180.0	180.0	180.0	180.0
H7-C5-C6-H1	0.0	0.0	0.0	0.0
H7-C5-C6-H8	180.0	180.0	180.0	180.0
C4-O10-C11-C17	0.0	0.0	0.0	0.0
C4-O10-C11-C18	-82.45	-63.07	-82.84	-61.31
C4-O10-C11-C19	40.48	59.24	40.09	59.00
H20-C12-O13-C3	180.0	180	180	180
H21-C12-O13-C3	-67.39	-61.34	66.29	-61.04
H22-C12-O13-C3	54.78	61.10	55.86	61.30

4.2 UV-Vis Absorption Spectra

On the basis of fully optimized ground-state structure, DFT-B3LYP levels with the basis sets 6-31+G(d,p) and 6-311++G(d,p) calculations have been performed to determine the low-lying excited states of 2,3,4-CDMB. The calculated result involving the vertical excitation energies, oscillation strength (*f*) and wavelength (λ_{max}) are carried out and compared with measured experimental wavelength listed in Table 2.1. The experimental and calculated UV-Vis spectra in different solvents are shown in Fig.2. Typically, according to Frank–Condon principle, the maximum absorption peak λ_{max} in UV–vis spectrum corresponds to vertical excitation [16].

For 2,3,4-CDMB the transitions are observed at wavelengths 318, 286 and 239 nm in acetone solvent, at 311, 283 and 239 nm in diethyl ether solvent and at 307, 281 and 243 nm in carbon tetra chloride solvent. The calculated transitions are obtained at wavelengths 328, 299, 285 nm in acetone solvent, at 331, 297, 283nm in diethyl ether solvent and at 335, 296 and 282nm in carbon tetra chloride solvent by using B3LYP/6-311++G(d,p). For the same compound at different level B3LYP/6-31+G(d,p) these transitions are obtained at wavelengths 330, 301, 286 nm in acetone solvent, at 332, 299 and 284 nm in diethyl ether solvent and at 336, 297 and 283 nm in carbon tetra chloride solvent. There are three values of wavelengths for each solvent. For each solvent the first wavelength corresponding to n $\rightarrow \pi^*$ and another two corresponding to $\pi \rightarrow \pi^*$ transitions [23,24].

For compounds 2,3,4-CDMB, there are shifts in wavelength of transition on changing the solvents. Among these three solvents Acetone is most polar and CCl_4 is least polar. Solvent effects: On increasing the polarity of solvent the n$\rightarrow \pi^*$ transition shifts towards lower wavelength (blue shift) and $\pi \rightarrow \pi^*$ shifts towards higher wavelength (red shift). On comparing the results of three solvents (Tables 2.1-2.3), the wavelength corresponding to first transition is lowest for acetone and highest for CCl_4, (i.e. shift towards lower wavelength on increasing the polarity of solvent) it is clear that first transitions represents n$\rightarrow \pi^*$, another two represent $\pi \rightarrow \pi^*$ [25]. We cannot say solvent effect completely according to experimental values as well as theoretical data. The absorption maxima values are fairly in good agreement with theoretical values.



(———Acetone, ———Carbon Tetra Chloride, ———Diethyl Ether)

Fig.2: Electronic Absorption spectra of 2,3,4-CDMB in different solvents.

The HOMO (Highest Occupied Molecular Orbital) energy characterizes the ability of electron giving, the LUMO (Least Unoccupied Molecular Orbital) characterizes the ability of electron accepting, and the gap between HOMO and LUMO characterizes the molecular chemical stability. The energy gap between the HOMOs and LUMOs is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. Both HOMO and LUMO are the main orbitals that take part in chemical stability [16,17]. The energy values of LUMO and HOMO and their energy gap reflect determines the kinetic stability, chemical reactivity and, optical polarizability and chemical hardness–softness of a molecule [23]. The molecule has a large energy gap is known as hard and having a small energy gap is known as soft molecule. The hard molecule is not more polarizable than the soft ones because they need big energy to excitation [23, 24]. The decrease in the HOMO and LUMO energy explains the Intramolecular charge transfer (ICT) interaction taking place within the molecule which is responsible for the activity of themolecule. The HOMO–LUMO energy separation has served as a simple measure of kinetic stability. A molecule with a small or no HOMO–LUMO gap is a chemically reactive [25, 26]. Pearson showed that the HOMO–LUMO gap represents the chemical hardness of the molecule [27, 28]. The energies of HOMO, LUMO,HOMO$_{-1}$ (Second Highest Occupied Molecular Orbital) and LUMO$_{+1}$ (Second Least Unoccupied Molecular Orbital) and corresponding energy gap in different solvents for 2,3,4-CDMB are calculated with the TD-DFT method and same basis sets and presented in Tables 2.2 and 2.3.

Table 2.1: Electronic absorption spectra of 2,3,4-CDMB [absorption wavelength λ_{max}(nm), excitation energy (eV), and oscillator strength (*f*)] using TD-DFT with B3LYP/ 6-31+G(d,p) and B3LYP/6-311++G(d,p) basis sets.

Solvents	Observed		Calculated						Assignments
			B3LYP/6-31+G(d,p)			B3LYP/6-311++G(d,p)			
	λ_{max}	E	λ_{max}	E	*F*	λ_{max}	E	*F*	
Acetone	323	3.90	330	3.77	0.00	328	3.78	0.00	$n \rightarrow \pi^*$
	294	4.34	301	4.12	0.14	299	4.15	0.14	$\pi \rightarrow \pi^*$
	242	5.19	286	4.32	0.29	285	4.35	0.28	$\pi \rightarrow \pi^*$
Diethyl Ether	317	3.99	332	3.74	0.00	331	3.75	0.00	$n \rightarrow \pi^*$
	291	4.39	299	4.15	0.13	297	4.17	0.13	$\pi \rightarrow \pi^*$
	241	5.19	284	4.35	0.28	283	4.38	0.29	$\pi \rightarrow \pi^*$
CCl4	312	4.04	336	3.70	0.00	335	3.71	0.00	$n \rightarrow \pi^*$
	286	4.42	297	4.17	0.14	296	4.19	0.14	$\pi \rightarrow \pi^*$
	246	5.11	283	4.38	0.29	282	4.39	0.29	$\pi \rightarrow \pi^*$

Table 2.2: Calculated Energy values (eV) of 2,3,4-CDMB by using TD-DFT/B3LYP/6-31+G(d,p).

Solvents	E_{HOMO}	E_{LUMO}	E_{HOMO-1}	E_{LUMO+1}	ΔE	∂E	E_{Total}(Hartree)
Acetone	-6.74	-2.19	-7.17	-0.89	4.55	6.28	-1034.25
Diethyl Ether	-6.75	-2.16	-7.17	-0.89	4.59	6.28	-1034.25
CCl_4	-6.75	-2.13	-7.16	-0.89	4.62	6.27	-1034.25

$\Delta E = E_{LUMO} - E_{HOMO}$, $\partial E = E_{LUMO+1} - E_{HOMO-1}$

Table 2.3: Calculated Energy values (eV) of 2,3,4-CDMB by using TD-DFT/B3LYP/6-311++G(d,p).

Solvents	E_{HOMO}	E_{LUMO}	E_{HOMO-1}	E_{LUMO+1}	ΔE	∂E	E_{Total}(Hartree)
Acetone	-6.80	-2.22	-7.22	-0.95	4.58	6.27	-1034.40
Diethyl Ether	-6.80	-2.18	-7.21	-095	4.62	6.26	-1034.40
CCl_4	-6.80	-2.15	-7.21	-0.95	4.65	6.26	-1034.40

$\Delta E = E_{LUMO} - E_{HOMO}$, $\partial E = E_{LUMO+1} - E_{HOMO-1}$

4.3 Non-Linear Optical (NLO) properties

Nonlinear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields [29, 16]. NLO is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for emerging technologies in the areas such as telecommunications, signal processing, and optical interconnections [30-33, 17-20]. Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore it is used frequently as a threshold value for comparative purposes.

The dipole moment μ, polarizability α and second-order polarizability or the first hyperpolarizability β, are calculated using HF and DFT with 6-31+G(d,p) and 6-311++G (d,p) basis sets on the basis of the finite-field approach. The complete equations for calculating the magnitude of total static dipole moment μ, the mean polarizability $\langle\alpha\rangle$, the anisotropy of the polarizability $\Delta\alpha$ and the mean first hyperpolarizability β_{Total} , using the *x, y, z* components from Gaussian 09W output is as follows:

The dipole moment $\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}$ (1)

The mean polarizability and anisotropy of polarizability respectively are defined by

$$\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{2}$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xz}^2 + \alpha_{xy}^2 + \alpha_{yz}^2)\right]^{\frac{1}{2}} \tag{3}$$

the mean first-order hyperpolarizability β_{Total} is defined as

$$\beta_{Total} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}} \tag{4}$$

Where $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$

$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$

$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$

Table 3: Nonlinear optical parameters (dipole moment, polarizability and first order hyperpolarizability) of 2,3,4-CDMB.

Parameters	6-31+G(d,p)		6-311++G(d,p)	
	HF	B3LYP	HF	B3LYP
Dipole Moments (Debye)				
μ_x	4.18	4.25	4.14	4.14
μ_y	-1.75	-1.80	-1.73	-1.74
μ_z	2.26	0.99	2.24	0.59
μ_{Total}	5.07	4.72	5.01	4.53
Polarizability (a.u.)				
α_{xx}	152.12	176.33	153.40	176.46
α_{xy}	-3.49	-2.05	-3.39	-1.87
α_{yy}	131.48	144.70	132.76	145.32
α_{xz}	-0.96	0.45	-0.81	0.47
α_{yz}	-1.49	-4.74	-1.22	-4.67

α_{zz}	71.89	80.00	73.20	81.04
$\langle\alpha\rangle$ **(esu)**	1.76 x 10^{-23}	1.98 x 10^{-23}	1.78 x 10^{-23}	1.99 x 10^{-23}
$\Delta\alpha$**(esu)**	1.07 x 10^{-23}	1.27 x 10^{-23}	1.07 x 10^{-23}	1.26x 10^{-23}
Hyperpolarizability (a.u.)				
β_{xxx}	-141.28	-30.62	-123.69	-681.83
β_{xxy}	-90.21	-129.60	-86.29	-101.86
β_{xyy}	-235.99	-389.79	-222.98	62.02
β_{yyy}	-66.46	-215.28	-50.41	-266.45
β_{xxz}	-35.97	19.03	-34.02	-11.94
β_{xyz}	-43.35	30.94	-41.49	6.30
β_{yyz}	-48.44	6.09	-50.69	21.75
β_{xzz}	-37.39	-5.04	-31.68	55.66
β_{yzz}	27.00	54.86	33.98	-37.70
β_{zzz}	-37.98	2.81	-50.41	8.94
β_{x}	-414.66	-425.46	-378.35	-564.15
β_{y}	-129.67	-290.01	-102.72	-406.01
β_{z}	-122.39	27.93	-135.12	18.75
$\beta_{Total}(esu)$	3.90 x 10^{-30}	4.455 x 10^{-30}	3.58 x 10^{-30}	6.01 x 10^{-30}

It is well known that the higher values of dipole moment, molecular polarizability, and hyperpolarizability are important for more active NLO properties [34,35]. The calculated value of dipole moment was found to be 4.53 Debye (B3LYP/6-311++G(d,p), 4.72 Debye (B3LYP/6-31+G(d,p), 5.01 Debye (HF/6-311++G(d,p) and 5.07 Debye (HF/6-31+G(d,p) for 2,3,4-CDMB. The highest value of dipole moment is observed for component μ_x for 2,3,4-CDMB at all levels of theory. The calculated values of dipole moment with all components are shown in Table 3.

The polarizabilities and first hyperpolarizability are reported in atomic units (a.u), the calculated values have been converted in to electrostatic units (esu) (α: 1 a.u =0.1482x10^{-12} esu, β: 1 a.u = 8.6393x10^{-33} esu).[47,48]

The mean polarizabilities$\langle\alpha\rangle$ and anisotropy of polarizability $\Delta\alpha$ are also included in Table 3 (molecules are in the xy plane). It is observed that the B3LYP/6-311++G(d,p) level of theory leads to higher $\langle\alpha\rangle$ in comparison to other applied methods. Moreover, addition of halogen atom or methyl group to the original molecules increases the mean polarizability; this is because the molecular charge distribution in the case of derivatives can be distorted more easily by an external electric field in comparison with the original molecules. The calculated values of $\langle\alpha\rangle$ are 1.99 x 10^{-23} esu (B3LYP/6-311++G(d,p), 1.98 x 10^{-23} esu (B3LYP/6-31+G(d,p) , 1.78 x 10^{-23} esu (HF/6-311++G(d,p) , 1.76 x 10^{-23} esu (HF/6-31+G(d,p) for 2,3,4-CDMB. Additionally, the anisotropy of the polarizability $\Delta\alpha$ of has been determined using ab initio and DFT methods. The calculated values are 1.26 x 10^{-23} and 1.27 x 10^{-23} esu (B3LYP), 1.07 x 10^{-23} esu (HF) for 2,3,4-CDMB.

The first static hyperpolarizability calculated values are presented in Table 3. The values of β_{total} is 6.01 x 10^{-30} esu with (B3LYP/6-311++G(d,p) for 2,3,4-CDMB respectively. The values of first static hyperpolarizability with all components are shown in Table 3. Urea is the prototypical molecule used in the study of the NLO properties of the molecular systems. Therefore urea was used frequently as a threshold value for comparative purposes. In this study, the calculated values are nearly 5-55 times that of urea (0.1947 × 10^{-30} esu). The large value of β calculated by the B3LYP and HF methods show that the studied compound is a good NLO material. The theoretical calculation of β components is very useful as this clearly indicates the direction of charge delocalization. The smallest β_{zzz} value indicates charge delocalization is along the bond axis and the involvement of σ orbitals in intra-molecular charge transfer process [36].

4.4 Thermodynamic Functions

The values of some thermodynamic parameters (such as zero-point vibrational energy, thermal energy, heat capacity, rotational constants, and entropy) of 2,3,4-CDMB molecule computed by using HF and B3LYP methods with basis sets 6-31+G(d,p) and 6-311++G(d, p) at 298K in ground state are listed in Table 4.1. The standard statistical thermodynamic functions: heat capacity, entropy, enthalpy and entropy for the title compound were obtained from the vibrational harmonic frequencies in temperature range 200-1500K and listed in Table 4.2. From Table 4.2, it can be observed that these thermodynamic functions are increasing with temperature ranging from 200 to 1500 K, which is attributed to the enhancement of molecular vibration while the temperature increase [37, 38]. These values of thermodynamic functions are plotted as a function of temperature. The variation of enthalpy function and heat capacity with absolute temperature 2,3,4-CDMB is shown in Figure 3a and 3b. These figures show that at very high temperature the influence of anharmonicity will make itself felt and will no longer give an accurate representation. The variation of free energy function and entropy function with temperature for 2,3,4-CDMB is shown in Figure 3c and 3d. The process of vaporization is accompanied by the increase in the disorder in the system [16, 39]. So as the temperature increases entropy increases, this is shown in Table 4.2 for the molecule under study. Results of the study reveal that free energy, enthalpy and entropy increases continuously with temperature while heat capacity initially increases with temperature and remain almost constant beyond a particular temperature [40-43]. At low temperatures only translational parts of motion gives its contribution but as temperature increases rotational and vibrational motions are excited [43-46]. Beyond a certain value of temperature (nearly at 1000 K) there is no further increase in molecular motion and therefore heat capacity becomes almost constant.

Table 4.1: The calculated thermodynamic parameters of 2,3,4-CDMB employing HF and B3LYP methods with 6-31+G(d,p) and 6-311++G(d,p) basis sets.

Thermodynamic Parameters (298 K)	6-31+G(d, p)		6-311++G(d,p)	
	HF	B3LYP	HF	B3LYP
Thermal Energy E_{Th} (kcal mol^{-1})				
Total	118.76	111.31	118.22	110.87
Electronic	0.00	0.00	0.00	0.00
Translational	0.89	0.89	0.89	0.89
Rotational	0.89	0.89	0.89	0.89
Vibrational	116.99	109.53	116.47	109.10
Heat Capacity at constant Volume C_v (cal mol^{-1}K^{-1})				
Total	43.70	46.52	43.75	46.60
Electronic	0.00	0.00	0.00	0.00
Translational	2.98	2.98	2.98	2.98
Rotational	2.98	2.98	2.98	2.98
Vibrational	37.74	40.56	37.79	40.64
Entropy S (cal mol^{-1}K^{-1})				
Total	111.81	115.56	111.87	115.39
Electronic	0.00	0.00	0.00	0.00
Translational	41.79	41.79	41.79	41.79
Rotational	31.52	31.56	31.51	31.56
Vibrational	38.51	42.21	38.57	42.05
Zero-point Vibrational Energy				
E_{vib} (kcal/mol)	110.96	102.99	110.41	102.57
Rotational Constants (GHz)				
X	1.15	1.12	1.15	1.12
Y	0.56	0.55	0.56	0.55
Z	0.39	0.39	0.39	0.39

Table 4.2: The experimental thermodynamic parameters (Cal/Mol-K) of 2,3,4-CDMB.

Temperature	Enthalpy	Heat capacity	Free Energy	Entropy
K	H	C_p	F	S
200	13.23	24.08	-107.41	120.63
300	18.79	35.52	-113.82	132.62
400	24.24	45.42	-119.98	144.23
500	29.35	53.87	-125.95	155.30
600	34.05	61.04	-131.72	165.77
700	38.35	67.17	-137.30	175.65
800	42.29	72.45	-142.68	184.97
900	45.90	77.01	-147.87	193.78
1000	49.21	80.92	-152.88	202.10
1100	52.25	84.30	-157.72	209.97
1200	55.05	87.22	-162.39	217.43
1300	57.62	89.74	-166.90	224.52
1400	60.01	91.94	-171.25	231.25
1500	62.19	93.84	-175.47	237.66

The variation of free energy function and entropy function for 2,3,4-CDMB have been shown in figure 3. These Figures show that in case of free energy function at temperature as high as 1000K, the effect is quite small. While in case of entropy at very high temperature the vibrational contribution is very small, compared to other contribution thus; statistical calculation of the entropy is much less dependent upon vibrational data than the other thermodynamic functions. This trend of variation of thermodynamic functions with temperature is similar to those reported by earlier researchers [47-51] for similar molecules. All the thermodynamic data supply helpful information for the further study on the substituted benzaldehydes. They can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and to determine directions of chemical reactions according to the second law of thermodynamics in thermo-chemical field [36].

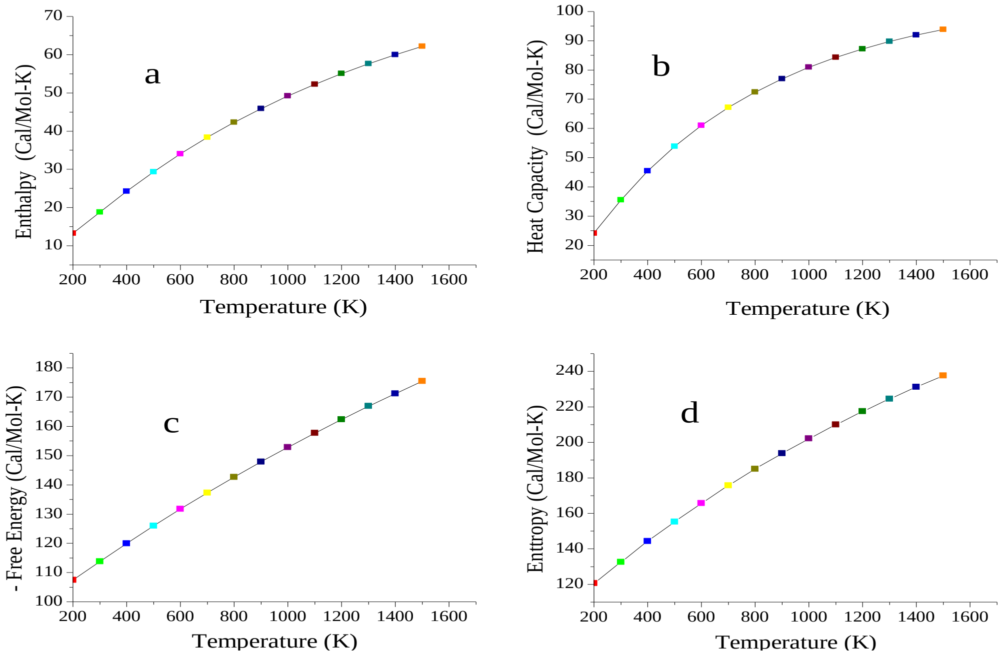


Fig. 3: The graph of thermodynamic functions versus temperature of 2,3,4 -CDMB.

5. Conclusion

In the present work, an attempt has been made on the experimental and theoretical UV-vis spectral studies, NLO properties and thermodynamic properties at various temperatures of industrially important 2,3,4-CDMB. Equilibrium geometries, electronic parameters and thermodynamic parameters of 2,3,4-CDMB have been analyzed at HF and DFT/B3LYP using 6-31+G(d,p) and 6-311G++(d,p) basis sets. The correlations between the thermodynamic parameters and temperature show the increase in the heat capacities, entropies and enthalpies with increasing temperature owing to the rise in intensities of the molecular vibrations. Overall, the TD-DFT calculations on the molecule provided deep insight into their electronic structures and properties. In addition, the calculated UV–Vis results and thermodynamic functions are all in good agreement with the experimental data. The lowering of HOMO–LUMO band gap supports bioactive property of the molecule. The predicted NLO properties show that the title compound is a good candidate as nonlinear optical material. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of nonlinear optics.

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