Research Journal of Recent Sciences ISSN 2277-2502
Vol. **2(ISC-2012),** 150-157 **(2013)** *Res.J.Recent.Sci.*

Electronic structure, Non-linear properties and Vibrational analysis of ortho, meta and para -Hydroxybenzaldehyde by Density Functional Theory

Hriday N. Mishra, Srivastava Rajesh Kumar, Narayan Vijay, Chand Satish, Sachan Alok Kumar, Shukla Vikas Kuamr, Prasad Onkar and Sinha Leena
Physics Department, University of Lucknow, Lucknow, INDIA

Available online at: www.isca.in
Received 1st December 2012, revised 26th December 2012, accepted 19th January 2013

Abstract

The present communication is aimed at comparing the molecular structural properties, vibrational and energetic data of ortho, meta and para hydroxybenzaldehyde, in gas phase, due to their commercial importance. The ground state properties of the title molecules have been calculated employing DFT/ B3LYP level of theory using the 6-311++G(d,p) basis set. The mean polarizability of all the three isomers are found to be nearly same in the range 88.415 to 90.933/a.u., but the dipole moment for ortho and meta hydroxybenzaldehyde are calculated to be 5.0201 and 4.9101 Debye whereas the dipole moment for para hydroxybenzaldehyde has slightly lower value at 3.4655 Debye. The first static hyperpolarizability of 'p'-hydroxybenzaldehyde is found to be 1.5 times higher to that of 'm'-hydroxybenzaldehyde and 5 times higher than 'o'-hydroxybenzaldehyde. MESP surfaces have also been drawn and compared. In order to obtain a complete description of molecular dynamics, vibrational wavenumber calculation along with the normal mode analysis, have been carried out at the DFT level. The calculated spectra of the molecules agree well with the experimental data.

Keywords: Polarizability, first static hyperpolarizability, hydroxybenzaldehyde, IR spectra.

Introduction

Benzaldehyde, the simplest representative of the aromatic aldehydes is a key intermediate for the processing of perfume and flavouring compounds and in the preparation of certain aniline dyes. Benzaldehyde can have carcinostatic or antitumor properties[1-3]. Hydroxybenzaldehyde, derivative of benzaldehyde, are used primarily as chemical intermediates for a variety of products. Out of the three isomers ortho, para and meta- Hydroxybenzaldehyde, otho- Hydroxybenzaldehyde (or salicylaldehyde) is used in the manufacture of coumarin. Coumarin is an important commercial chemical used in soaps, flavors and fragrances, and electroplating. Recently it has been shown that the incorporation of the benzaldehyde increases the activity of the benzaldehyde-thiosemicarbazone which exhibits high anti-trypanosomal potential[4]. Although much work has been done on benzaldehyde and its derivatives[5-9], however a comprehensive comparative study of ortho, para and meta-hydroxybenzaldehyde on electronic structure, non-linear properties along with the detailed potential energy distribution of normal modes of vibrations has not been reported so far. The present communication is aimed at comparing the molecular structural properties, vibrational and energetic data of 'o'-hydroxybenzaldehyde, 'p'-hydroxybenzaldehyde and 'm'-hydroxybenzaldehyde, in gas phase, due to their commercial importance. The structure and the ground state energy of the molecules under investigation has been analyzed employing DFT / B3LYP level. The optimized geometry and their properties such as equilibrium energy, frontier orbital energy gap, dipole moment and vibrational frequencies along with the electrostatic potential maps have also been used to understand the activity of the isomers of Hydroxybenzaldehyde.

Methodology

Structure and Spectra: The optimized molecular structures of 'o'- hydroxybenzaldehyde, 'p'-hydroxybenzaldehyde and 'm'-hydroxybenzaldehyde are given in figure 1. The theoretically calculated IR spectra have been given in figure 2. The calculated IR spectra of the molecules agree well with the experimental spectral data reported by the NIST web book[10].

Computational Details: The molecules under investigation have been analyzed with density functional theory (DFT)[11], employing Becke's three parameter hybrid exchange functionals[12] with Lee-Yang-Parr correlation functionals (B3LYP)[13,14]. All the calculations were performed using the Gaussian 09 program[15]. As the DFT hybrid B3LYP functional tends to overestimate the fundamental normal modes of vibration, a scaling factor of 0.9679[16] has been applied. By combining the results of the Gaussview's program package[17] with symmetry consideration, vibrational frequency assignments were made with a high degree of accuracy. For the precise vibrational assignments, the normal modes have also been analyzed using the VEDA 4 program[18].

The DFT was also used to calculate the dipole moment, mean polarizability ‹α› and the total first static hyperpolarizability β[19,20]. Following Buckingham's definitions[21], the total dipole

moment and the mean polarizability in a Cartesian frame is defined by

$\mu = (\mu^2_x + \mu^2_y + \mu^2_z)^{1/2}$

$\langle\alpha\rangle = 1/3[\ \alpha_{xx} + \alpha_{yy} + \alpha_{zz}\ ]$

The total intrinsic hyperpolarizability $\beta_{TOTAL}{}^{22}$ is defined as

$\beta_{TOTAL} = [\beta^2_x + \beta^2_y + \beta^2_z\ ]^{1/2}$

$= [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + [(\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$

The β components of Gaussian output are reported in atomic units.

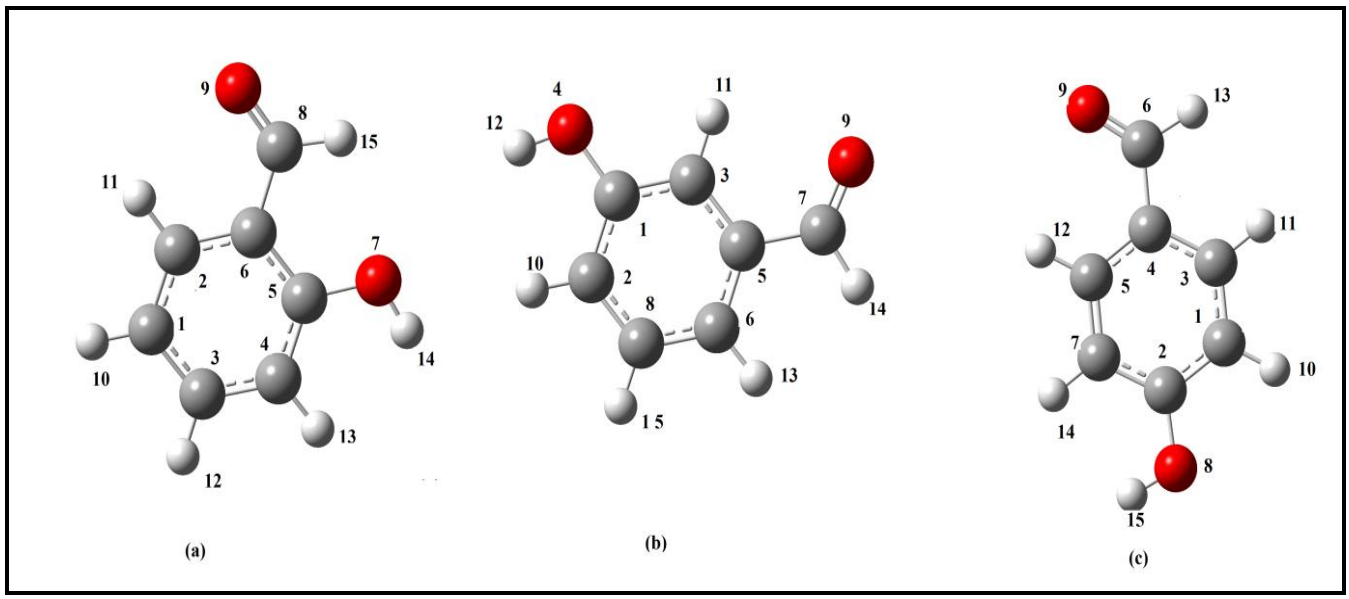

Figure-1
Optimized structures of (a)'o' Hydroxybenzaldehyde (b) 'm' Hydroxybenzaldehyde (c) 'p' Hydroxybenzaldehyde

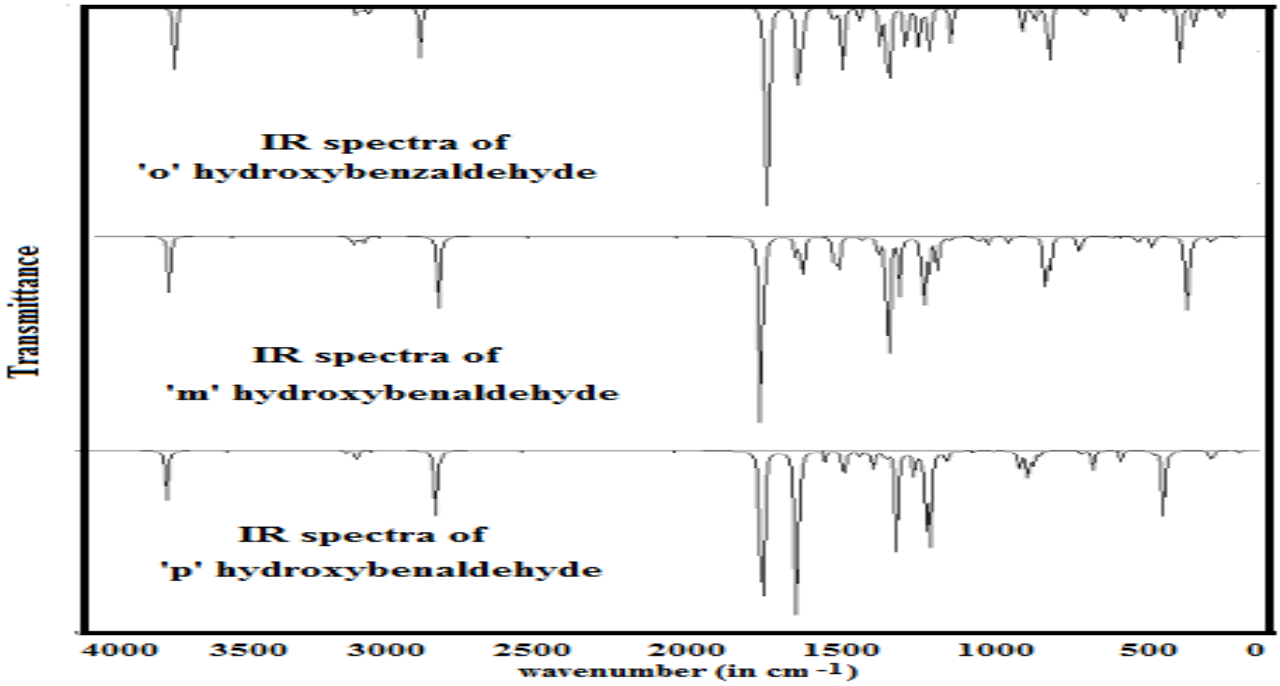

Figure-2
Theoretical IR spectra of ortho, meta and para Hydroxybenzaldehyde

Results and Discussion

Molecular geometry optimization and energies: The structures of 'o'- hydroxybenzaldehyde, 'p'-hydroxybenzaldehyde and 'm'-hydroxybenzaldehyde have been optimized to compare the variation in electronic and non-linear properties on substitution of hydroxyl (OH) group at ortho, para and meta positions. The equilibrium geometry optimization for three isomers has been achieved by energy minimization, using DFT at the B3LYP level, employing the split valence basis set 6-311++G(d,p). The optimized molecular structures with numbering scheme of three molecules are shown in figure 1. The ground state optimized parameters are reported in table 1. As the calculated vibrational spectra have no imaginary frequency, the optimized geometry is confirmed to be located at the local minima on potential energy surface. The C-H/C-C bond lengths vary in the range 1.083 Å-1.086 Å/1.386 Å-1.481 Å, 1.083 Å-1.086 Å/1.391 Å-1.400 Å and 1.083 Å-1.086 Å/1.385 Å-1.402 Å (standard value 1.10 Å/1.40 Å) in ortho, meta and para hydroxybenzaldehyde respectively. The C-O/C=O bond lengths for three molecules are calculated to be 1.365 Å/1.214 Å, 1.366 Å/1.210 Å and 1.360 Å/1.213 Å which are close to standard value 1.359 Å /1.208 Å[23].

Electronic properties: The most important orbitals in a molecule are the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These orbitals determine the way the molecule interacts with other species. The frontier orbital gap helps characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule[24]. The frontier orbital gaps of 'o'-hydroxybenzaldehyde/ 'm'-hydroxybenzaldehyde/ 'p'-hydroxybenzaldehyde are to be 0.17723/0.17229/0.18304 a.u. which clearly shows that 'm'-hydroxybenzzaldehyde is most reactive among the three isomers. The 3D plot of HOMO, LUMO and MESP are shown in figure 3 and 4 respectively. The HOMO in three molecules is distributed over entire molecule except the carbon and hydrogen atom of aldehyde group. The LUMO's show more anti-bonding character than the HOMO's. The oxygen atom of the hydroxyl group contribute to the LUMO, only in case of 'o'-hydroxybenzaldehyde. The importance of MESP is that it shows the size, shape as well as positive, negative and neutral electrostatic potential in terms of colour grading. It is also very useful to correlate the molecular structure with its physiochemical property relationship[25-29]. The MESP in case of 'o'-hydroxybenzaldehyde shows three distinct electron rich sites including the aromatic ring, the MESP of meta and para show two strong electronegative, whereas a small negative potential at the aromatic ring site.

Table 1
Parameters corresponding to optimized geometry of Ortho-meta- and para- Hydroxybenzaldehyde at B3LYP/6-311++G(d,p) level of theory

Parameter	ortho	meta	para
Ground state energy (in Hartree)	-420.915	-420.916	-420.919
Dipole moment (in Debye)	5.0201	4.9101	3.4655
Frontier orbital energy gap (in Hartree)	0.1772	0.1723	0.1830
Polarizability/a.u.	88.4153	89.357	90.933

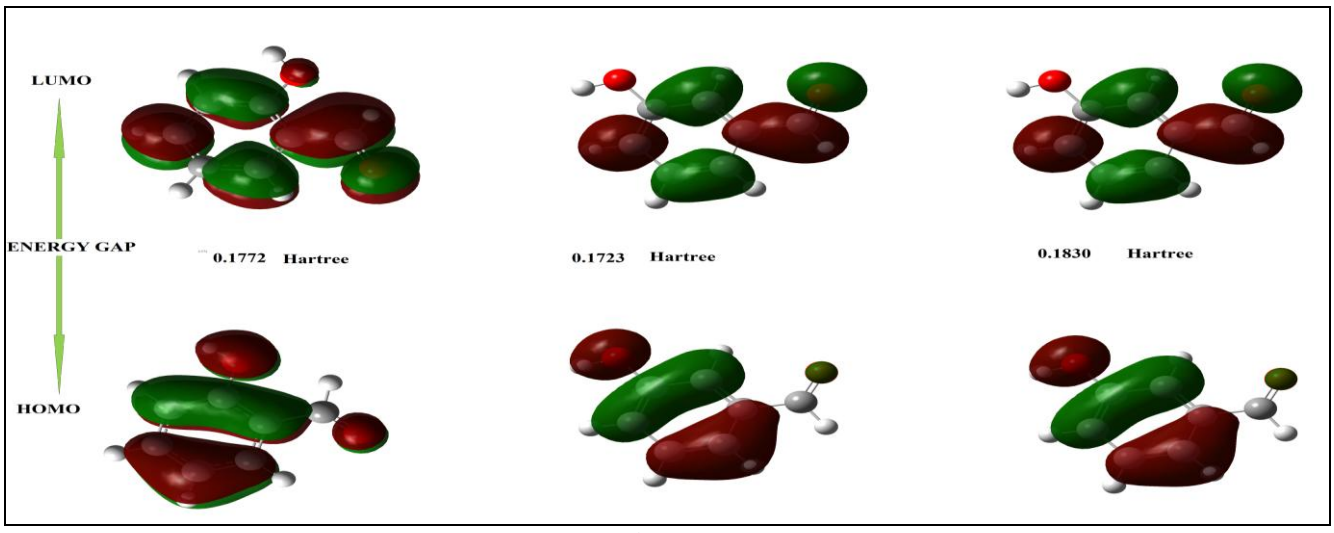

Figure-3
Homo Lumo orbitals and energy gap of 'o', m' and 'p' Hydroxybenzaldehyde

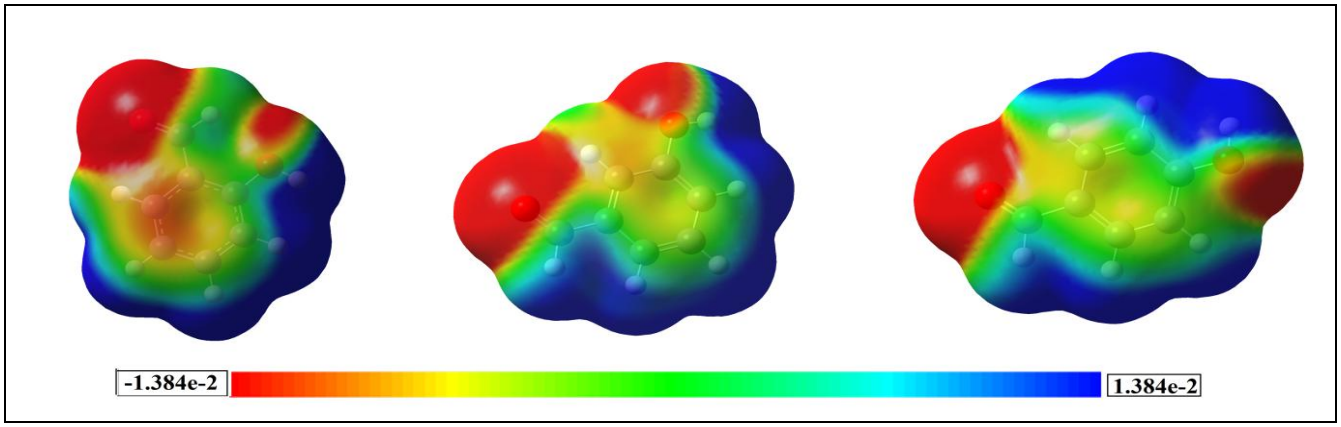

Figure-4
MESP map of 'o', m' and 'p' Hydroxybenzaldehyde

Electric moments: The dipole moment in a molecule is another important electronic property that results from non-uniform distribution of charges on the various atoms in a molecule. It is mainly used to study the intermolecular interactions involving the van der Waal type dipole-dipole forces, etc., because higher the dipole moment, stronger will be the intermolecular interactions. The calculated dipole moment for three molecules is given in table 1. Table 1 show that the calculated value of dipole moment in case of 'o'-hydroxybenzaldehyde and 'm' are nearly equal and quite higher than 'p'-hydroxybenzaldehyde.

The determination of electric polarizability and hyperpolarizability is of basic importance to study the phenomenon induced by intermolecular interactions, simulation studies and nonlinear optical effects. The values of polarizability and hyperpolarizability calculated at the same level of theory and the same basis set for the title molecules, can provide a reasonable comparison of these quantities, in the absence of experimental data. Although the mean polarizability of 'o', 'm'- and 'p' hydroxybenzaldehyde is found to be almost same the total intrinsic hyperpolarizability β_{TOTAL} of para isomer is fairly larger as compared to the other two counterparts (table 2).

Table 2
All β components and β total of Hydroxybenzaldehyde at B3LYP/6-311++G(d,p)

β components	Ortho	Meta	Para
β_{XXX}	-149.5	340.2	100.2
β_{XXY}	-36.1	-33.4	-31.2
β_{XYY}	90.5	129.6	-98.2
β_{YYY}	216.5	-179.8	864.3
β_{XXZ}	0	0	0
β_{XYZ}	0	0	0
β_{YYZ}	0	0	0
β_{XZZ}	-47.7	-14.5	15.8
β_{YZZ}	-58.5	-63.1	-4.8
β_{ZZZ}	0	0	0
β_{TOTAL}	162.0	532.6	828.5

Vibrational assignments: The experimental and computed vibrational wave numbers and the detailed description of each normal mode of vibration of three molecules, carried out in terms of their contribution to the total potential energy are given in table 3, 4 and 5. The calculated harmonic wavenumbers are usually higher than the corresponding experimental quantities because of the combination of electron correlation effects and basis set deficiencies. These discrepancies are taken care of either by computing anharmonic corrections explicitly or by introducing scalar field or even by direct scaling of the calculated wavenumbers with a proper scaling factor[30, 31]. The vibrational wavenumbers are calibrated accordingly with scaling factor 0.9679 for DFT at B3LYP. The vibrational assignments have been done on the basis of relative intensities, line shape, the VEDA 4 program and the animation option of Gaussview 5.0.

C=O and C-O vibrations: The appearance of a strong band in IR spectra around 1650-1800 cm^{-1} in aromatic compound shows the presence of C=O stretching motion. The C=O stretch of aldehyde group in 'o'-Hydroxybenzaldehyde/ 'm'-Hydroxybenzaldehyde / 'p'-Hydroxybenzaldehyde is calculated at to be at 1697/1713/1703 cm^{-1} and is assigned well with the experimental IR peak at 1672/1728/1779 cm^{-1}. The other strong band observed at 1227/1290/1241 cm^{-1} is due to C-O stretching vibration of the (C-OH) bond whose general position is 1000-1200 cm^{-1}. This band is calculated at 1224/1289/1250 cm^{-1} for 'o'-hydroxybenzaldehyde / 'm'-hydroxybenzaldehyde / 'p'-hydroxybenzaldehyde.

OH vibrations: The strong band calculated at 3710 /3711/3705 cm^{-1} in IR spectra of 'o'-hydroxybenzaldehyde/ 'm'-hydroxybenzaldehyde/ 'p'-hydroxybenzaldehyde shows the presence of OH group. These bands contribute 100% to the total PED (experimental value 3892/3202 for 'o'-hydroxybenzaldehyde / 'm'-hydroxybenzaldehyde). The small discrepancy between the calculated and the observed wavenumber may be due to the intermolecular hydrogen bond. The bands observed at 1178, 1149/1290,1178,1155/1520 cm^{-1} in IR spectra of 'o'-hydroxybenzaldehyde/ 'm'-

hydroxybenzaldehyde/ 'p'-hydroxybenzaldehyde are due to H-O-C in-plane bending and are calculated at 1183,1150/1284,1164,1147/1490 cm^{-1} as mixed modes.

Ring modes: The phenyl ring spectral region predominantly involves the C-H, C-C and C=C stretching, and C-C-C, H-C-C and bending vibrations. Very intense band are found in the range 3100-3000 cm^{-1} which is, in general, observed in the case of aromatic compounds due to aromatic C-H stretching vibrations. The C-C stretching modes are observed as mixed modes in the wavenumber range 1600- cm^{-1} to 1000 cm^{-1} for three molecules and are in good agreement with general appearance of C-C stretching modes. The modes appearing below 1000 cm^{-1} are mixed modes. The torsional modes appear in general in the low wavenumber regions.

Table-3
Theoretical and Experimental wave-numbers (in cm^{-1}) of 'o'-Hydroxybenzaldehyde

Calc. unsc. wave no.	Calc. sc. wave no.	*Exp. Wave no.	Assignment of dominant modes in order of decreasing potential energy distribution (PED)
3833	3710	3892	ν(O7-H14)(100)
3198	3095		ν(C1-H10)(52)+ν(C2-H11)(37)+ν(C3-H11)(11)
3187	3085		ν(C2-H11)(54)+ν(C3-H12)(31)+ν(C1-H10)(13)
3176	3074	3074	ν(C3-H12)(49)+ν(C1-H10)(35)+ν(C2-H11)(10)
3152	3051		ν(C4-H13)(90)
2972	2877	2847	ν(C8-H15)(100)
1753	1697	1672	ν(C8-O9)(87)
1644	1591	1580	ν(C4-C5)(36)+ν(C2-C1)(22)
1627	1575	1551	ν(C3-C1)(26)+ν(C6-C2)(14)+β(C6-C2-C1)(10)+β(C3-C1-C2)(11)+β(C5-C4-C3)(10)
1520	1471	1488	β(H10-C1-C2)(17)+β(H11-C2-C6)(18)+β(H13-C4-C5)(24)
1488	1440	1459	ν(C6-C20)(12)+β(H10-C1-C3)(20)+β(H12-C4-C5)(21)
1430	1384	1381	β(H15-C8-O9)(81)
1357	1313	1323	ν(C2-C1)(20)+ν(C4-C3)(18)+β(H14-C7—C5)(20)+β(H11-C2-C6)(12)
1328	1285	1280	ν(C6-C2)(16)+β(H11-C2-C6)(15)+β(H13-C4-C5)(12)
1265	1224	1227	ν(C6-C2)(16)+ν(O7-C5)(38)
1222	1183	1178	ν(C2-C1)(17)+ν(C8-C6)(30)+β(C6-C2-C1)(11)+β(H14-O7-C5)(15)+β(H10-C1-C2)(12)
1188	1150	1149	β(H12-C3-C1)(11)+ν(C5-C4)(10)+β(H14-O7-C5)(27)+β(H13-C4-C5)(25)
1181	1143	1115	β(H13-C4-C5)(12)+β(H10-C1-C3)(24)+β(H11-C2-C6)(13)+β(H12-C3-C4)(30)
1107	1071		ν(C5-C4)(11)+β(C6-C2-C1)(18)+β(H14-C7-C5)(10)+β(H10-C1-C3)(11) +β(H12-C3-C4)(12)
1058	1024	1033	ν(C4-C3)(14)+ν(C3-C1)(40)+β(H11-C2-C6)(12)+β(H133-C4-C5)(20)
1028	995	1009	ω(C-H)ring(80)
993	961	980	ω(C-H)ring(91)
960	929	946	ω(C-H)ring (85)+ρ(C5-C4-C3-C1)(12)
856	828	883	ν(O7-C5)(16)+ν(O8-C6)(14)+β(C3-C1-C2)(24)+β(C5-C4-C3)(10)
851	824	859	ω(C-H)ring (76)+ρ(C5-C4-C3-C1)(10)
815	789		ν(C6-C2)(11)+β(C6-C2-C1)(10)+β(O9-C8-C6)(21)+β(C3-C1-C2)(10)
765	740	757	ρ(H10-C1-C3-C4)(34)+ρ(H12-C3-C4-C5)(27)+ρ(H13-C4-C5-C6)(19)
701	678	665	ρ(H13-C4-C5-C6)(13)+ρ(C5-C4-C3-C1)(18)+ρ(C6-C2-C3-C1)(19)+ρ(O7-C5-C6-C8)(23)
641	620	641	β(O9-C8-C6)(23)+β(C4-C3-C1)(34)+β(C5-C4-C3)(17)
556	538		ν(C7-C5)(13)+β(O9-C8-C6)(25)+β(C5-C4-C3)(16)+β(07-C5-C4)(19)
534	517		ρ(C6-C2-C1-C3)(28)+ρ(O7-C5-C4-C3)(18)+ρ(O7-C5-C6-C6)(19)

Table - 4
Theoretical and Experimental wave-numbers (in cm^{-1}) of 'm'-Hydroxybenzaldehyde

Calc. unsc. wave no.	Calc. sc. wave no.	*Exp. wave no.	Assignment of dominant modes in order of decreasing potential energy distribution (PED)
3834	3711	3203	ν(O4-H12)(100)
3203	3100	2973	ν(C3-H11)(99)
3189	3087		ν(C8-H15)(75)+ν(C6-H13)(15)+ν(C2-H10)(10)
3170	3068		ν(C6-H13)(79)+ν(C8-H15)(17)
3153	3052		ν(C2-H10)(91)
2893	2800	2737	ν(C7-H14)(99)
1770	1713	1728	ν(C7-O9)(89)
1648	1595		ν(C1-C3)(36)+ν(C6-C8)(10)+ν(C8-C2)(10)+β(H12-O4-C1)(15)
1627	1574	1584	ν(C8-C2)(18)+ν(C6-C5)(30)+β(C2-C8-C6)(11)+β(C1-C3-C5)(10)
1513	1464	1504	β(H11-C3-C5)(14)+β(H13-C6-C5)(16)+β(H15-C8-C6)(27)
1501	1452		ν(C1-C3)(11)+ν(C8-C6)(11)+ν(C5-C3)(18)+β(H10-C2-C8)(17)
1419	1373	1365	β(H14-C7-O9)(78)
1361	1317		ν(C1-C3)(13)+ν(C2-C8)(20)+ν(C8-C2)(18)+ν(C5-C3)(21)
1327	1284	1290	ν(O4-C1)(11)+β(C2-C8-C6)(10)+β(H12-C4-C1)(17)+β(H10-C2-C8)(17) +β(H11-C3-C5)(11)+β(H13-C6-C8)(20)
1285	1244	1250	ν(C6-H5)(11)+ν(C4-C1)(24)+β(H11-C3-C5)(11)+β(H13-C6-C8)(12)
1203	1164	1178	ν(C1-C3)(13)+β(H12-O4-C1)(38)+β(H15-C8-C6)(29)
1185	1147	1155	ν(C8-C6)(10)+β(H12-O4-C1)(19)+β(H10-C2-C8)(23)+β(H15-C8-C6)(18)
1153	1116		ν(O4-C1)(12)+ν(C7-C5)(23)+β(H11-C3-C5)(31)+β(H13-C6-C8)(13)
1108	1072	1086	ν(C8-C6)(12)+ν(C8-C2)(23)+β(H13-C6-C8)(31)+β(H10-C2-C8)(13)
1023	990	1000	ω(C-H)ring(65)+ρ(O9-C7-C5-C3)(32)
1012	980		β(C6-C5-C3)(32)+β(C6-C8-C2)(13)+β(C2-C1-C3)(14)+ν(C1-C3)(14)+ν(C6-C5)(10)
979	948	948	β(C8-C6-C5)(17)+ν(C7-C5)(15)+ν(O4-C1)(13)+β(H11-C3 C5)(11)
964	933	897	ω(C-H)ring(72)+ ρ(C2-C8-C6-C5)(13)
906	877	874	ω(C-H)ring(71)
883	855		ω(C-H)ring(89)
778	753	782	ρ(H15-C8-C6-C5)(28)+ρ(H10-C2-C8-C6)(25)+ρ(H13-C6-C8-C2)(21)
764	739	707	β(C8-C6-C5)(25) +β(O9-C7-C5)(15)+ ν(O4-C1)(10)
662	641	656	ρ(C1-C2-C3-C6)(29)+ρ(C2-C8-C6-C5)(29)+ρ(C6-C8-C5-C3)(18)
657	636		β(C6-C5-C3)(36)+ β(C2-C8-C6)(29)+β(O9-C7-C5)(18)
555	537		ρ(O4-C1-C2-H10)(54)+ρ(C3-C5-C7-O9)(18)
540	523		β(C5-C6-C8)(42)+ β(C2-C1-C3)(33)
457	442		β(C7-C5-C6)(39)+ β(O4-C1-C2)(37)

Table-5
Theoretical and Experimental wave-numbers (in cm^{-1}) of 'p'-Hydroxybenzaldehyde

Calc. unsc. wave no.	Calc. sc. wave no.	* Exp. wave no.	Assignment of dominant modes in order of decreasing potential energy distribution (PED)
3828	3705		ν(O8-H15)(100)
3199	3096		ν(C1-H10)(94)
3194	3091		ν(C5-H12)(95)
3163	3061		ν(C3-H12)(95)
3153	3052	3047	ν(C7-H14)(96)
2884	2791		ν(C6-H13)(99)
1759	1703	1779	ν(O9-C6)(85)
1642	1589	1596	ν(C5-H7)(30)+ν(C1-C2)(20)
1625	1573		ν(C1-C2)(25)+ν(C4-C3)(22)
1539	1490	1520	β(H11-C3-C4)(14)+β(H12-C5-C7)(14)+β(H15-O8-C2)(12)+β(H14-C7-C5)(17) +β(C1-C2-C7)(13)
1470	1423	1419	ν(C3-C1)(15)+ν(C5-C7)(11)+β(H10-C1-C3)(12)
1418	1372	1388	β(H13-C6-O9)(73)
1372	1328	1317	ν(C3-C1)(12)+ν(C5-C7)(19)+ν(C4-C3)(12)+ν(C7-C2)(13)+β(H15-O8-C2)(20) +β(H11-C3-C4)(10)
1328	1285	1287	ν(C4-C3)(12)+β(H11-C3-C4)(17)+β(H12-C5-C7)(17)+β(H14-C7-C5)(16)
1291	1250	1241	ν(C2-O8)(52)+ν(C3-C1)(10)
1233	1193	1216	ν(C6-C4)(32)+ β(H10-C1-C3)(12)+ β(C4 –C3-C1)(10)
1193	1155	1165	β(H15-O8-C2)(55)+ β(H14-C7-C5)(13)+ν(C7-C2)(12)
1177	1139		β(H10-C1-C3)(19)+ β(H11-C3-C4)(19)+ β(H12-C5-C7)(20)
1123	1087	1109	ν(C3-C1)(14)+ν(C5-C7)(10)+ β(H10-C1-C3)(18)+ β(H11-C3-C4)(12)+ β(H12-C5-C7)(21)+ β(H14-C7-C5)(12)
1024	991		ρ(H13-C6-C4-C3)(74)+ρ(O9-C6-C4-C3)(10)
1023	990		β(C3-C1-C2)(41)+β(C4-C5-C7)(39)
979	948		ω(C-H)ring(84)
951	920		ω(C-H)ring(63)+ρ(C4-C3-C1-C2)(15)
865	837	835	β(C1-C2-C7)(19)+β(C4-C5-C7)(19)+ν(C4-C5)(18)
836	809	785	ω(C-H)ring(88)
828	801	719	ω(C-H)ring(80)
794	769		ν(C8-C2)(15)+β(O9-C6-C4)(18)+β(C1-C2-C7)(10)+β(C4-C3-C1)(25)
690	668		ρ(C3-C1-C2-C7)(12)+ ρ(C5-C7-C2-C1)(16)+ ρ(C4-C3-C2-C1)(34)+ ρ(O8-C2-C7-C5)(16)
653	632	648	β(C2-C1-C3)(32)+β(C4-C5-C7)(40)
614	594	602	β(C5-C7-C2)(11)+β(O9-C6-C4)(37)+β(C1-C2-C7)(11)
513	497	511	ρ(H11-C3-C4-C5)(12)+ρ(C3-C1-C2-C7)(11)+ρ(O8-C2-C1-C3)(41)

Note :Abbreviations used here have following meaning- ν: stretching; β: in plane bending; ρ : torsion; ω: wagging.
* http://webbook.nist.gov/chemistry/form-ser.html

Conclusion

In the present work we have calculated the geometric parameters, the vibrational frequencies, frontier orbital band gap, MESP surfaces and the non-linear optical properties of 'o', 'm' and 'p' Hydroxybenzaldehyde using DFT/ B3LYP method. The higher frontier orbital energy gap and the lower dipole moment values make the 'p'-Hydroxybenzaldehyde less reactive and less polar, hence most stable among the three isomers. A good agreement between experimental and calculated normal modes of vibrations has been observed.

NLO behavior of the title molecules were investigated by the determination of the polarizability and the first hyperpolarizability using the DFT/B3LYP/6-311G(d,p) method. The polarizability values are almost the same but the para isomer has significantly higher values for the total hyperpolarizability.

Acknowledgements- The Authors (OP and LS) are grateful to University Grants commission for financial support and Prof. M.H. Jamroz for providing his VEDA 4 software.

References

1. Andersen A, Final report on the safety assessment of benzaldehyde, *Int J. Toxicol*, **(25 Suppl 1),** 11-27, **(2006)**

2. Liu Y., Sakagami H., Hashimoto K., Kikuchi H., Amano O., Ishihara M., Kanda Y., Kunni S., Kochi M., Zhang W., Yu G.,

Tumor-specific Cytotoxicity and Type of Cell Death Induced by, -Cyclodextrin Benzaldehyde Inclusion Compound, *Anticancer Research*, **(28)**, 229-236 **(2008)**

3. Takeuchi S., Kochi M., Sakaguchi K., Nakagawa K. and Mizutani T., Benzaldehyde as a Carcinostatic Principle in Figs, *Agric Biol Chem*, **(42)** 1449-1451 **(1978)**

4. Haraguchi S.K., Silva A.A., Vidotti G.J., Santos P.V. and Garcia F.P., Antitrypanosomal Activity of Novel Benzaldehyde-Thiosemicarbazone Derivatives from Kaurenoic Acid, *Molecules*, **(16)** 1166-1180 **(2011)**

5. Itoh T., Akai N. and Ohno K., *Journal of Molecular Structure*, (**786),** 39-45 **(2006)**

6. Strand T.G., Tafipolsky M.A., Vilkov L.V. and Volden H.V., The molecular structure of *ortho*- and *meta*-fluorobenzaldehyde by joint analysis of gas electron diffraction, microwave spectroscopy and ab initio molecular orbital calculations, *Journal of Molecular Structure*, **(443),** 9-16 **(1998)**

7. Bock E. and Tomchuk E., Electric Moments and Conformations of ortho-, meta-, and para-Fluorobenzaldehyde, *Canadian Journal of Chemistry*, **(50)** 2890- 2891 **(1972)**

8. Anderson P.D.J., Fernandez M.T., Pocsfalvi G. and Mason R.S., Thermodynamics of gas phase proton transfer reactions involvingsubstituted Benzaldehydes, *J.Chem.Soc., Perkin Trans*, 2**(5),** 873-880 **(1997)**

9. Anjaneyulu A. and Rao G.R., Vibrational analysis of substituted benzaldehydes: Part I. Vibrational spectra, normal co-ordinate analysis and transferability of force constants of monohalogenated benzaldehydes *Spectrochim. Acta Part A*, **(55)**, 749-760 **(1999)**

10. http://webbook.nist.gov/chemistry/form-ser.html **(2012)**

11. Kohn W. and Sham L.J., Self-consistent equations including exchange and correlation effects, *Phys. Rev*., **(140)** 1133–1138 **(1965)**

12. Becke A.D., Density functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, **(98)** 648– 5652 **(1993)**

13. Lee C., Yang W., Parr R.G., Development of the Colle Salvetti correlation- energy formula into a functional of the electron density, *Phys. Rev*., **(37),** 785–789 **(1998)**

14. Miehlich B., Savin A., Stoll A. and Preuss H., Results obtained with the correlation energy density functional of Becke and Lee, Yang and Parr, *Chem. Phys. Lett.*, **(157),** 200–206 **(1989)**

15. Frisch M.J. et. al. Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford CT **(2009)**

16. Scott A.P. and Random L., Harmonic vibrational frequencies: An evaluation of Hartree–Fock, Møller– Plesset, quadratic configuration interaction, density functional theory, and semiempirical scale factors, *J. Phys.Chem.- US*, **(100)**, 16502-16513 **(1996)**

17. Denington II, Roy, Keith T., Millam J., Eppinnett K. Hovell W.L. and Gilliland, R., *Gauss View, Version 3.07 Semichem, Inc., Shawnee Mission, KS* **(2003)**

18. Jamroz M.H., Vibrational Energy Distribution Analysis: VEDA 4 program, Warsaw **(2004)**

19. Kleinman D.A., Nonlinear dielectric polarization in optical media, Phys. Rev. **(126)** 1977–1979 **(1962)**

20. Pipek J. and Mezey P.Z., A fast intrinsic localization procedure applicable for ab initio and semiempirical linear combination of atomic orbital wave functions, *J. Chem. Phys*, **(90)** 4916–4926 **(1989)**

21. Buckingham A.D., Permanent and induced molecular moments and long-range intermolecular forces, *Adv. Chem. Phys*, **(12)** 107–142 **(1967)**

22. Kanis D.R., Ratner M.A. and Marks T.J., Design and Construction of Molecular Assemblies with Large Second-Order Optical Nonlinearities. Quantum Chemical Aspects, *Chem. Rev*., **(94),** 195- 242 **(1994)**

23. Sykes P., A Guidebook to Mechanism In Organic Chemistry. pp 15, Sixth Edition, Longman Publishing Group **(1986)**

24. Fleming I., Frontier Orbitals and Organic Chemical Reactions (John Wiley and Sons, New York **(1976)**

25. Murray J.S. and Sen K., Molecular Electrostatic Potentials, Concepts and Applications, Elsevier, Amsterdam **(1996)**

26. Alkorta I. and Perez J.J., Molecular polarization potential maps of the nucleic acid bases, *Int. J. Quant. Chem*., **(57)** 123–135 **(1996)**

27. Scrocco E. and Tomasi J., Advances in Quantum Chemistry, **(2)**, P. Lowdin, ed., Academic Press, New York **(1978)**

28. Luque F.J., Orozco M., Bhadane P.K. and Gadre S.R., SCRF calculation of the effect of water on the topology of the molecular electrostatic potential, *J. Phys. Chem*., **(97)** 9380–9384 **(1993)**

29. Sponer J. and Hobza P., DNA base amino groups and their role in molecular interactions: Ab initio and preliminary density functional theory calculations, *Int. J. Quant. Chem*, **(57)** 959–970 **(1996)**

30. Scott A.P. and Random L., Harmonic vibrational frequencies: An evaluation of Hartree–Fock, Møller–Plesset, quadratic configuration interaction, density functional theory and semiempirical scale factors, *J. Phys. Chem.,* **(100),** 16502–16513 **(1996)**

31. Pulay P., Fogarasi G., Pongor G., Boggs J.E. and Vargha A., Combination of theoretical ab initio and experimental information to obtain reliable harmonic force constants. Scaled quantum mechanical (QM) force fields for glyoxal, acrolein, butadiene, formaldehyde, and ethylene, *J. Am. Chem. Soc.*, **(105),** 7037–7047 **(1983)**