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Optimization, First order hyperpolarizibility studies of *o*, *m* and *p*-Cl benzaldehydes by using DFT studies.

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Abstract: In this paper, we have first optimized the structures of Cl benzaldehydes by using Gaussian 09 software with the B3LYP/631-G' (d,p) basis set. The title compound's polarizability and hyperpolarizabilities values have been computed, along with an examination of its nonlinear optical characteristics. The title molecule's total initial static hyperpolarizability as determined by DFT studies may be a topic for future NLO content that is appealing.

1. Introduction:

Due to the potential future uses in photonics and optoelectronics like optical communication, optical computing, optical data storage, optical switching, and dynamic image processing [1–4], Non Linear Optical (NLO) materials have received a lot of interest in recent years [5–9]. Organic NLO materials are excellent because of their adaptability and ability to get modified for specific device applications. In comparison with inorganic NLO materials, organic NLO materials exhibit a higher nonlinear figure-of-merit for frequency conversion, a higher laser damage threshold, and a faster optical reaction time [10]. The structure of organic NLO materials is based on the -bond system extended over a large length scale of the molecule. This system, known as the push-pull system; is easily manipulated by substituting electron donating and electron withdrawing groups to the aromatic moieties. This results in increased optical non-linearity of the system [11]. Future optoelectronic and nonlinear optical applications hold great promise for the chloro substituted benzaldehyde derivatives with strong optical nonlinearities.

The important role of benzaldehyde and its derivatives have attracted high attention in both chemistry and biology [12–14]. Many spectroscopic investigations have been performed on benzaldehyde & its derivatives [15–42] and got interested to spectroscopies of halogen derived benzaldehydes. By using matrix isolation IR spectroscopy, it has been demonstrated that the trans and cis conformers of o- and m-chlorobenzaldehydes exists [43]. Although there has been a lot of research on substituted benzaldehydes, there is still lack of a thorough analysis of chloro benzaldehydes on electronic structure properties. Using B3LYP/6-31G' (d, p), basis set, the molecular structure, geometric parameters, chloro-benzaldehyde is estimated in the current work. It has been possible to determine information about charge transport inside the molecule by HOMO-LUMO research. Molecular Electrostatic Potential (MEP) has also been investigated.

2. Computational details:

The DFT computation of chloro-benzaldehydes had been carried out using the Gaussian 09 programme package at B3LYP 6-31G' (d,p) basic set. The optimized structural characteristics were assessed for use in various parameters.

3. Results and discussion:

3.1. Molecular geometry:

The titled compound’s optimized geometric structure is shown in **Fig. 1**. and **Table 1 (a-c)** shows the optimized bond lengths, bond angles, and dihedral angles determined

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using DFT-B3LYP level with 6-31G'(d,p), basis sets. All compounds has C1 point group symmetry element.

Figure 1. Molecular structure with atom numbering of *o, m* and *p*-Cl benzaldehydes.

Table 1. a: Optimized geometrical parameters of *o*-chlorobenzaldehyde.

Bond	Bond length(Å)	Bond angle	Value (in^0)	Torsional angle	Value (in^0)
R(1,2)	1.3892	A(2,1,6)	121.242	D(6,1,2,3)	0.0
R(1,6)	1.4055	A(2,1,10)	121.7052	D(6,1,2,11)	180.0001
R(1,10)	1.0868	A(6,1,10)	117.0528	D(10,1,2,3)	-180.0
R(2,3)	1.3987	A(1,2,3)	119.5208	D(10,1,2,11)	0.0
R(2,11)	1.0867	A(1,2,11)	120.2455	D(2,1,6,5)	-0.0001
R(3,4)	1.3949	A(3,2,11)	120.2337	D(2,1,6,8)	-180.0001
R(3,12)	1.0873	A(2,3,4)	120.4875	D(10,1,6,5)	180.0
R(4,5)	1.3948	A(2,3,12)	120.2509	D(10,1,6,8)	0.0
R(4,13)	1.0856	A(4,3,12)	119.2615	D(1,2,3,4)	0.0
R(5,6)	1.4043	A(3,4,5)	119.3706	D(1,2,3,12)	180.0
R(5,7)	1.7638	A(3,4,13)	120.9615	D(11,2,3,4)	179.9999
R(6,8)	1.489	A(5,4,13)	119.668	D(11,2,3,12)	-0.0001
R(8,9)	1.2133	A(4,5,6)	121.2421	D(2,3,4,5)	0.0
R(8,14)	1.1071	A(4,5,7)	117.5979	D(2,3,4,13)	-180.0
		A(6,5,7)	121.16	D(12,3,4,5)	180.0
		A(1,6,5)	118.137	D(12,3,4,13)	0.0
		A(1,6,8)	118.1085	D(3,4,5,6)	0.0
		A(5,6,8)	123.7545	D(3,4,5,7)	-180.0
		A(6,8,9)	123.0545	D(13,4,5,6)	-180.0
		A(6,8,14)	115.7743	D(13,4,5,7)	0.0
		A(9,8,14)	121.1712	D(4,5,6,1)	0.0001
				D(4,5,6,8)	180.0001
				D(7,5,6,1)	180.0
				D(7,5,6,8)	0.0
				D(1,6,8,9)	0.0021
				D(1,6,8,14)	-180.0019
				D(5,6,8,9)	180.0021
				D(5,6,8,14)	-0.0019

Table 1. b: Optimized geometrical parameters of *m*-chlorobenzaldehyde.

Bond	Bond length (Å)	Bond angle	Value (in ^{0})	Torsional angle	Value (in ^{0})
R(1,2)	1.3911	A(2,1,6)	119.6855	D(6,1,2,3)	-0.0001
R(1,6)	1.4024	A(2,1,10)	121.7567	D(6,1,2,11)	-180.0001
R(1,10)	1.0862	A(6,1,10)	118.5579	D(10,1,2,3)	179.9999
R(2,3)	1.3993	A(1,2,3)	120.4224	D(10,1,2,11)	-0.0001
R(2,11)	1.0871	A(1,2,11)	120.2862	D(2,1,6,5)	0.0001
R(3,4)	1.3957	A(3,2,11)	119.2915	D(2,1,6,8)	180.0001
R(3,12)	1.0857	A(2,3,4)	119.3431	D(10,1,6,5)	-180.0
R(4,5)	1.3927	A(2,3,12)	120.8467	D(10,1,6,8)	0.0001
R(4,7)	1.7585	A(4,3,12)	119.8101	D(1,2,3,4)	0.0001

R(5,6)	1.4003	A(3,4,5)	121.0311	D(1,2,3,12)	180.0001
R(5,13)	1.0872	A(3,4,7)	119.4578	D(11,2,3,4)	180.0001
R(6,8)	1.4847	A(5,4,7)	119.5111	D(11,2,3,12)	0.0001
R(8,9)	1.2113	A(4,5,6)	119.1364	D(2,3,4,5)	0.0
R(8,14)	1.1145	A(4,5,13)	120.3919	D(2,3,4,7)	-180.0
		A(6,5,13)	120.4717	D(12,3,4,5)	180.0
		A(1,6,5)	120.3815	D(12,3,4,7)	0.0
		A(1,6,8)	120.2737	D(3,4,5,6)	0.0
		A(5,6,8)	119.3448	D(3,4,5,13)	-180.0001
		A(6,8,9)	124.351	D(7,4,5,6)	180.0
		A(6,8,14)	114.4592	D(7,4,5,13)	0.0
		A(9,8,14)	121.1898	D(4,5,6,1)	0.0
				D(4,5,6,8)	-180.0
				D(13,5,6,1)	-180.0
				D(13,5,6,8)	0.0
				D(1,6,8,9)	-0.0004
				D(1,6,8,14)	180.0009
				D(5,6,8,9)	-180.0004
				D(5,6,8,14)	0.0009

Table 1. c: Optimized geometrical parameters of *p*-chlorobenzaldehyde.

Bond	**Bond length (Å)**	**Bond angle**	**Value (in ^{0})**	**Torsional angle**	**Value (in ^{0})**
R(1,2)	1.3896	A(2,1,6)	120.3956	D(6,1,2,3)	-0.0001
R(1,6)	1.4034	A(2,1,10)	121.0573	D(6,1,2,11)	-180.0001
R(1,10)	1.0867	A(6,1,10)	118.5472	D(10,1,2,3)	180.0
R(2,3)	1.3997	A(1,2,3)	118.9399	D(10,1,2,11)	-0.0001
R(2,11)	1.0856	A(1,2,11)	121.1629	D(2,1,6,5)	0.0
R(3,4)	1.3963	A(3,2,11)	119.8973	D(2,1,6,8)	180.0001
R(3,7)	1.7547	A(2,3,4)	121.6657	D(10,1,6,5)	-180.0
R(4,5)	1.3933	A(2,3,7)	119.1476	D(10,1,6,8)	0.0
R(4,12)	1.0854	A(4,3,7)	119.1867	D(1,2,3,4)	0.0001
R(5,6)	1.4005	A(3,4,5)	118.6961	D(1,2,3,7)	-179.9999
R(5,13)	1.0887	A(3,4,12)	120.0761	D(11,2,3,4)	180.0001
R(6,8)	1.4813	A(5,4,12)	121.2278	D(11,2,3,7)	0.0001
R(8,9)	1.2123	A(4,5,6)	120.6123	D(2,3,4,5)	0.0
R(8,14)	1.1148	A(4,5,13)	119.7285	D(2,3,4,12)	-180.0
		A(6,5,13)	119.6591	D(7,3,4,5)	180.0
		A(1,6,5)	119.6904	D(7,3,4,12)	0.0
		A(1,6,8)	120.1889	D(3,4,5,6)	0.0
		A(5,6,8)	120.1207	D(3,4,5,13)	-180.0
		A(6,8,9)	124.4964	D(12,4,5,6)	180.0
		A(6,8,14)	114.3928	D(12,4,5,13)	0.0
		A(9,8,14)	121.1107	D(4,5,6,1)	0.0
				D(4,5,6,8)	-180.0
				D(13,5,6,1)	-180.0
				D(13,5,6,8)	0.0
				D(1,6,8,9)	-0.0005
				D(1,6,8,14)	180.0009
				D(5,6,8,9)	-180.0004
				D(5,6,8,14)	0.0009

3.2. NLO:

The first order hyperpolarizability (β_{tot}), and its components, as well as the total molecule polarizability (α_{tot}), and its components, were calculated using the DFT/B3LYP/6-31G' level of theory. Non-linear optical (NLO) effects can be measured using first order hyperpolarizability. A common molecule employed in the NLO characteristics of molecular systems is urea. As a result, it was widely utilized as a comparison threshold value.

According to DFT calculations, the titled compound's dipole moment and first order hyperpolarizability are calculated to be 3.1243, 1.8918, 2.1276 Debye respectively and 155.86 x 10-30 cm^5/esu, 240.86 x 10-30 cm^5/esu, 820.22 x 10-30 cm^5/esu respectively.

As a result, we observe that the (α_{tot}), and (β_{tot}), values for titled compounds are higher than the equivalent threshold values for urea. The extent of the first order hyperpolarizability leads to the conclusion that titled compounds may be considered as a potential applicant in the development of NLO material.

Table 2. a: Dipole moment (μ_{tot}), polarizibility (α_{tot}), hyperpolarizibility (β_{tot}) of *o*-Cl benzaldehyde.

Dipole moment		**Polarizability**		**Hyperpolarizability**	
μx	-2.7695	**αxx**	111.140	**βxxx**	40.2453
μy	-1.4438	**αyy**	-0.255	**βyyy**	133.6728
μz	0.0824	**αzz**	103.61	**βzzz**	-11.011
μ	3.1243	**αxy**	-0.00066	**βxyy**	43.186
		αxz	-0.0010	**βxxy**	0.789
		αyz	32.396	**βxxz**	-0.558
		α0	71.49	**βxzz**	-2.142
				βyzz	-2.189
				βyyz	-2.265
				βxyz	-0.0012
				β0	155.86

Table 2. b: Dipole moment (μ_{tot}), polarizibility (α_{tot}), hyperpolarizibility (β_{tot}) of *m*-Cl benzaldehyde.

Dipole moment		**Polarizability**		**Hyperpolarizability**	
μx	**1.4781**	**αxx**	124.426	**βxxx**	239.0
μy	1.1778	**αyy**	-0.6923	**βyyy**	-47.06
μz	0.0825	**αzz**	93.120	**βzzz**	-95.58
μ	1.8918	**αxy**	-0.0022	**βxyy**	-22.57
		αxz	0.0005	**βxxy**	-1.57
		αyz	32.4588	**βxxz**	-0.927
		α0	72.28	**βxzz**	-0.31
				βyzz	6.567
				βyyz	0.346
				βxyz	-0.0004
				β0	240.81

Table 2. c: Dipole moment (μ_{tot}), polarizibility (α_{tot}), hyperpolarizibility (β_{tot}) of *p*-Cl benzaldehyde.

Dipole moment		**Polarizability**		**Hyperpolarizability**	
μx	**-1.1977**	**αxx**	136.97	**βxxx**	769.984
μy	1.7566	**αyy**	0.4221216	**βyyy**	74.092
μz	0.0824	**αzz**	85.6294302	**βzzz**	-9.208
μ	2.1276	**αxy**	0.0019948	**βxyy**	47.957
		αxz	-0.0008	**βxxy**	-1.515
		αyz	32.4628691	**βxxz**	-1.127
		α0	74.34	**βxzz**	-0.737
				βyzz	-2.664
				βyyz	2.678
				βxyz	-0.0004
				β0	820.22

3.3. Molecular Electrostatic Potential analysis:

For analyzing and predicting molecular behavior, the molecular electrostatic potential (MEP), which is produced by the nuclei and electrons and is viewed as static distributions of charge reacting in a particular manner, the investigation benefits greatly by the studies of molecular electrostatic mapping (MEP) mapping. In regard to the molecular structure connect with its physiochemical properties [44–47]. The possibility has been especially helpful as an indication of active areas or places on a molecule is shown with specific colors. Initially, electrophile attracts, and it has also been successfully used in the investigation of interactions involving a certain optimal reactants' relative orientation [48]. MEP usually reflects its values onto the molecular electron to create a visual density.

The MEP plot of the titled compounds material demonstrates that the oxygen atoms of the carbonyl have the greatest negative potential and are the main active nucleophilic centers, respectively, whereas the chlorine atoms have the negative potential (blue color).

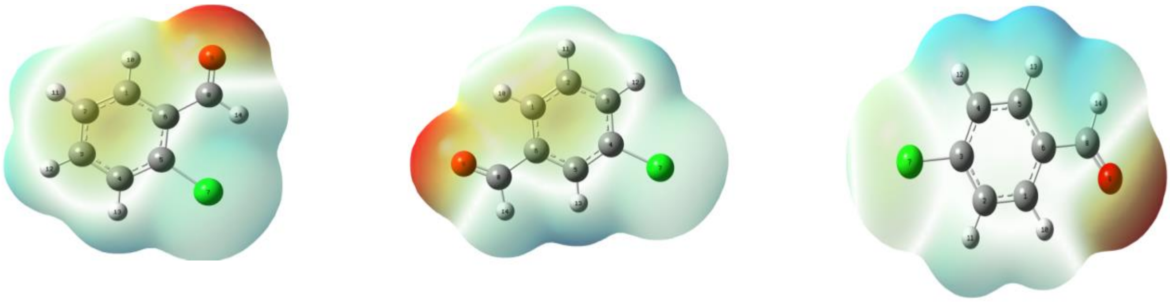

Figure 2. Molecular electrostatic potential (MEP) map of title compounds calculated at B3LYP/6-31G' (d, p) level.

4. Conclusion

The structural characteristics of titled compounds have been explained theoretically by using B3LYP/6-31G' (d,p) techniques. The NBO outcome displays the transmission of charges inside the molecules. According to the MEP map, the hydrogen and chlorine atoms were on the positive potential site, whereas the negative potential sites are on the oxygen atoms in the aldehyde group.

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