



# DFT BASED INVESTIGATIONS OF PHYSICO-CHEMICAL PROPERTIES AND QUANTUM MECHANICAL CALCULATIONS OF PENTACHLOROBENZALDEHYDES

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**ABSTRACT:** Substituted benzaldehydes are the simple aromatic aldehydes and their derivatives are widely used in different industries such as dyes, flavouring, artificial flavours, solvents etc. they also exhibit different biological activities. Due to these reasons, there exist a vast scope of study of substituted benzaldehydes, in this light pentachlorobenzaldehyde is reported for study. The quantum mechanical calculations are performed with the help of Gaussian 09W program package using the Becke-3Lee-Yang-Parr (B3LYP) functional supplemented with the standard 6-31G (dp) basis set. The thermodynamic properties are discussed with the different thermodynamic properties obtained in the temperature range 200K-1500K. Frontier molecular orbitals (HOMO-LUMO) and molecular electro-static potentials (MESP) are also studied.

**Key words:** Pentachlorobenzaldehyde, Gaussian 09W, Becke-3Lee-Yang-Parr (B3LYP), Thermodynamic properties, HOMO-LUMO, MESP.

**Introduction:** Substituted benzaldehydes are the simplest type of aromatic compounds which have a wide range of uses in different fields. They are used as artificial flavouring agents and solvents for oils etc. they exhibit anti-tumour activities and other biological activities. [1,2]. Lot of research work has been carried out by a number of researchers for different types of investigations [3-6] In this light I have performed density functional theory (DFT) calculations of different parameters of the compound Pentachloro benzaldehyde (further referred as PCB). The calculations were carried out by Gaussian 09 program package.[7]

## Results and Discussion:

**Basic Properties:** Various physical and chemical properties of PCB are shown in table 1

Table 1

1.	Molecular Formula	$C_7HCl_5O$
2.	Formula Weight	278.34700
3.	Index of Refraction	1.633
4.	Density	1.73 g/cm <sup>3</sup>
5.	Boiling Point:	328.8°C at 760mmHg
6.	Vapour Pressure:	0.000186mmHg at 25°C
7.	Flash Point:	138.5°C
8.	Polar Surface Area:	17.1 Å <sup>2</sup>
9.	Monoisotopic Mass	275.847003

**Molecular Structure:** The molecular structure of the mentioned compound PCB is shown in Figure 1. The optimized bond lengths, bond angles and dihedral angles of the compound is calculated by B3LYP method using B3LYP 6-311+G (d,p) basis sets are listed in Table 2 is in accordance with atom numbering scheme as shown in Fig. 1. Since the exact crystal structure of the compound BMB is not available till now, the optimized structure can only be compared with other similar system for which the crystal structures have been solved.

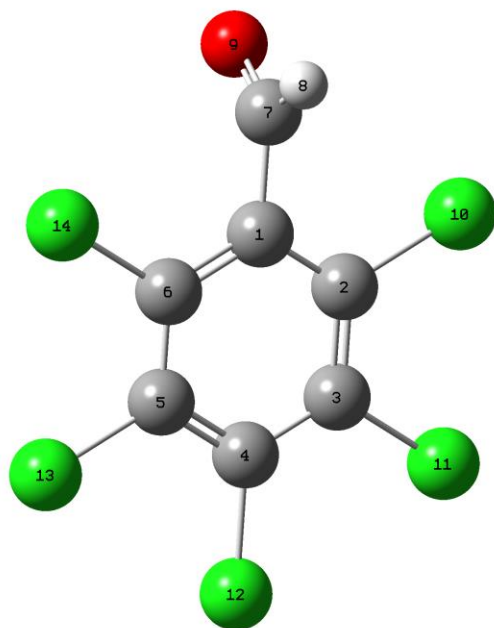


Figure 1

Table 2

S.NO.	Bond between Atoms	Bond Length (Å <sup>o</sup> )	Bond Angle between Atoms	Bond Angle (°)	Dihedral Angle between Atoms	Dihedral Angle (°)
1.	R (1,2)	1.3952	A (2,1,6)	119.9985	D (6,1,2,3)	0.0323
2.	R (1,6)	1.3948	A (2,1,7)	119.9972	D (6,1,2,10)	179.9532
3.	R (1,7)	1.54	A (6,1,7)	120.0043	D (7,1,2,3)	-179.9729
4.	R (2,3)	1.3947	A (1,2,3)	120.0086	D (7,1,2,10)	-0.052
5.	R (2,10)	1.76	A (1,2,10)	119.9808	D (2,1,6,5)	0.0149
6.	R (3,4)	1.3954	A (3,2,10)	120.0106	D (2,1,6,14)	179.9892
7.	R (3,11)	1.76	A (2,3,4)	119.9942	D (7,1,6,5)	-179.9798
8.	R (4,5)	1.3951	A (2,3,11)	120.0128	D (7,1,6,14)	-0.0055
9.	R (4,12)	1.76	A (4,3,11)	119.993	D (2,1,7,8)	-89.9606
10.	R (5,6)	1.3951	A (3,4,5)	119.994	D (2,1,7,9)	90.0394
11.	R (5,13)	1.76	A (3,4,12)	119.9811	D (6,1,7,8)	90.0341
12.	R (6,14)	1.76	A (5,4,12)	120.0249	D (6,1,7,9)	-89.9659
13.	R (7,8)	1.07	A (4,5,6)	120.0047	D (1,2,3,4)	-0.0568
14.	R (7,9)	1.2584	A (4,5,13)	120.0113	D (1,2,3,11)	179.9619
15.			A (6,5,13)	119.984	D (10,2,3,4)	-179.9777
16.			A (1,6,5)	120.0	D (10,2,3,11)	0.041
17.			A (1,6,14)	120.008	D (2,3,4,5)	0.0341
18.			A (5,6,14)	119.992	D (2,3,4,12)	-179.9964
19.			A (1,7,8)	119.8865	D (11,3,4,5)	-179.9846
20.			A (1,7,9)	120.2269	D (11,3,4,12)	-0.0151
21.			A (8,7,9)	119.8865	D (3,4,5,6)	0.0131
22.					D (3,4,5,13)	-179.9995
23.					D (12,4,5,6)	-179.9563
24.					D (12,4,5,13)	0.0311
25.					D (4,5,6,1)	-0.0376
26.					D (4,5,6,14)	179.9881
27.					D (13,5,6,1)	179.975
28.					D (13,5,6,14)	0.0007

**VIBRATIONAL SPECTRA:** A detailed study of vibrational spectra has been carried out of the reported compound and the vibrational frequencies have been calculated using DFT-B3LYP level with 6-31++G(d,p), the results obtained are shown in table 3, these results shows vibrational frequencies, infrared and Raman activities.

Table 3

Mode	Frequency	Infrared	Raman Activity
1.	51.09	1.3456	0.1237
2.	63.99	0.1348	0.0519
3.	84.56	1.3256	0.1623
4.	114.13	14.0965	2.3062
5.	176.19	2.5278	0.5341
6.	203.14	1.1644	2.4147
7.	214.11	0.0081	2.5885
8.	222.48	0.3591	5.7270
9.	230.55	0.2142	7.2362
10.	265.45	2.7178	0.6418
11.	322.68	0.9403	12.5800
12.	323.86	0.5274	20.5044
13.	351.77	2.3276	53.0553
14.	354.50	0.3519	0.0808
15.	366.53	0.4260	0.2435
16.	375.12	0.9040	2.0539
17.	501.69	76.1934	5.5698
18.	618.02	87.9197	0.2958
19.	649.15	0.0112	0.0726
20.	649.88	63.7482	1.8605
21.	666.78	0.0460	0.1155
22.	764.34	20.5755	5.6769
23.	829.84	0.2996	1.5946
24.	843.57	0.1052	0.1645
25.	917.99	111.3656	12.5138
26.	1066.84	0.9461	11.7978
27.	1122.63	73.7587	2.9641

28.	1209.97	241.7884	162.2935
29.	1297.71	13.2752	8.5205
30.	1343.25	336.1551	3.0910
31.	1353.80	29.6122	9.0321
32.	1469.51	1.2434	7.0786
33.	1542.28	38.6196	150.5722
34.	1562.53	170.1458	402.4081
35.	1713.55	214.9313	118.9772
36.	3068.76	62.4185	225.0609

The corresponding plots of infrared and Raman activities are shown in figure 2 and 3 respectively.

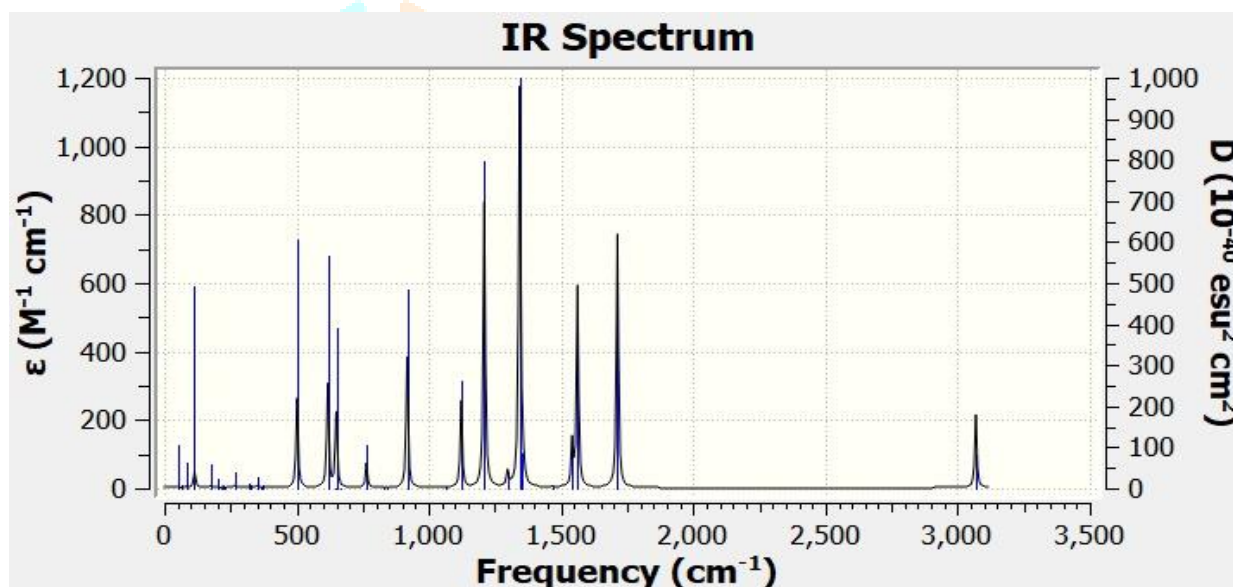


Figure 2

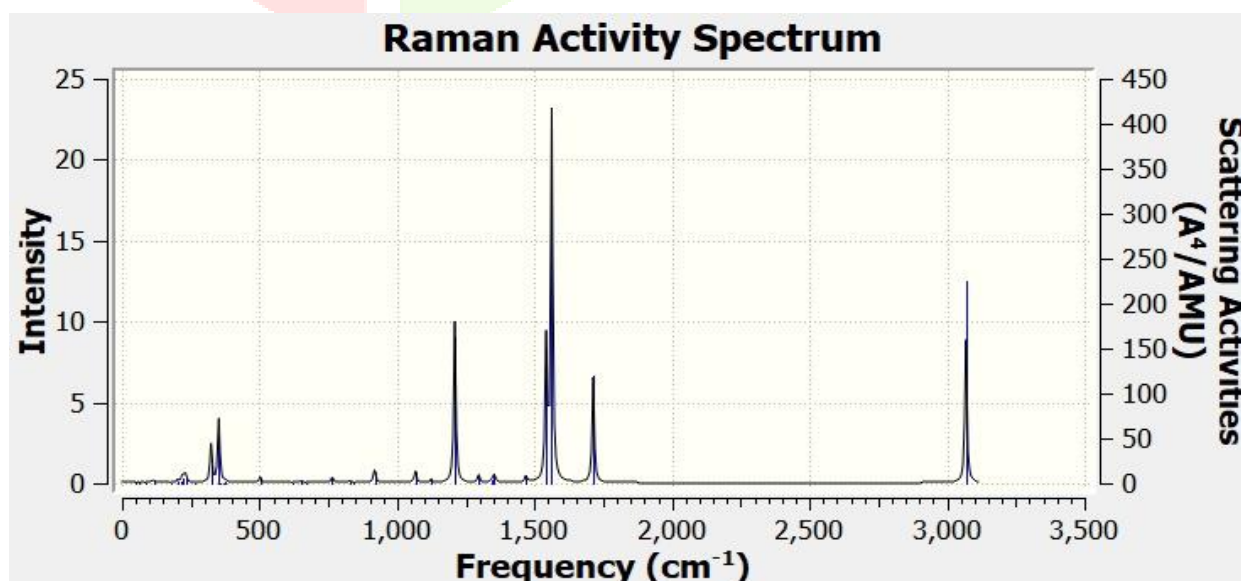


Figure 3

**Vibrational Assignments:**

**C-Cl Vibrations:** The C-Cl stretching mode has been assigned at  $1055\text{ cm}^{-1}$  in 5-chloro-2,4-dimethoxy aniline [8], 2,4,5,6-tetrachloro pyrimidine [9] and at  $1062\text{ cm}^{-1}$  in 2-chloro-6-floro benzaldehyde [10], in present study this assignment is visible at  $1066.84\text{ cm}^{-1}$ .

**C-C Vibrations:** The group of four bands, appearing between  $1400\text{--}1650\text{ cm}^{-1}$  in the spectra of substituted benzenes represents the characteristics skeletal stretching modes, these correspond to doubly degenerate C-C stretching vibrations of benzene at  $1560\text{ cm}^{-1}$  and  $1485\text{ cm}^{-1}$  modes with the calculated value of  $1593.10\text{ cm}^{-1}$ . There are two more C-C stretching modes as  $1310\text{ cm}^{-1}$  and  $989\text{ cm}^{-1}$  of benzene. In present study  $1469.51\text{ cm}^{-1}$  shows fair agreement with earlier studies, similarly C-C stretching vibration of benzene ring at  $1562.63\text{ cm}^{-1}$  is seen for PCB.

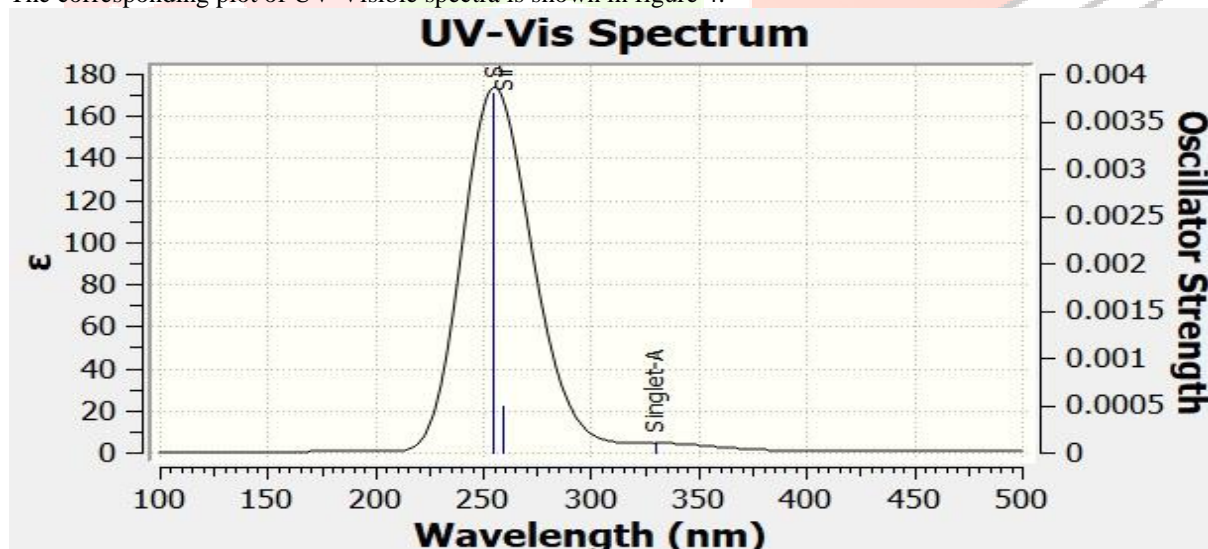
**Aldehyde Group Vibrations:** The aldehyde group gives rise to six vibrations, namely C=O stretching, C=O in plane bending, C=O out-of-plane bending, C-H stretching, C-H in-plane bending and C-H out-of-plane bending vibrations. The C=O stretching vibrations gives rise to a prominent absorption in the region  $1600\text{--}1815\text{ cm}^{-1}$ , here  $1713.55\text{ cm}^{-1}$  corresponds to C=O stretching.

**UV-Visible Spectra:** TD-DFT calculations provides better understanding of observed electronic absorption spectrum in terms of Excitation energies (E), absorption wavelength ( $\lambda$ ), oscillator strengths (f), molecular orbitals undergoing transitions, transition energy, electronic transitions etc. Molecular orbitals undergoing excitation transition, transition energy and excitation energy, absorption wavelength etc are shown in in Table 4.

**Table 4**

Excited state	Excitation Energy (E)	Absorption Wavelength ( $\lambda$ )	Oscillator Strength (f)	Excitation Transition (MO)	Transition Energy (MO) Singlet A
1	3.7629 eV	329.49 nm	f=0.0001	66 -> 69 67 -> 69	-0.34814 0.60599
2	4.7770 eV	259.54 nm	f=0.0005	68 -> 70	0.69786
3	4.8651 eV	254.85 nm	f=0.0038	66 -> 69 66 -> 72 67 -> 69 67 -> 72 68 -> 71	-0.14547 -0.24730 -0.10688 -0.33047 -0.54180

The corresponding plot of UV-Visible spectra is shown in figure 4.

**Figure 4**

**Thermodynamical Properties:** Thermodynamic properties help to understand energetics, structural and reactivity properties of a molecule. Frequency calculations were used to compute the zero-point energies, thermal correction to internal energy and entropy as well as heat capacity, table 5 and 6 shows thermodynamical functions and thermodynamical properties respectively for PCB as calculated by DFT/ B3LYP level with 6-31++G(d,p).



Table 5

Thermodynamic Functions	Value
Zero-point correction	0.061394 (Hartree/Particle)
Thermal correction to Energy	0.073844
Thermal correction to Enthalpy	0.074788
Thermal correction to Gibbs Free Energy	0.020656
Sum of electronic and zero-point Energies	-2630.528797
Sum of electronic and thermal Energies	-2630.516347
Sum of electronic and thermal Enthalpies	-2630.515403
Sum of electronic and thermal Free Energies	-2630.569534

Table 6

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	46.338	42.842	113.930
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	42.743
Rotational	0.889	2.981	33.244
Vibrational	44.560	36.881	37.943
Vibration 1	0.596	1.976	4.651
Vibration 2	0.598	1.970	4.260
Vibration 3	0.601	1.959	3.745
Vibration 4	0.607	1.938	3.197
Vibration 5	0.628	1.872	2.373
Vibration 6	0.639	1.835	2.104
Vibration 7	0.644	1.819	2.006
Vibration 8	0.648	1.806	1.937
Vibration 9	0.653	1.794	1.872
Vibration 10	0.671	1.737	1.629
Vibration 11	0.708	1.629	1.294
Vibration 12	0.709	1.627	1.289
Vibration 13	0.729	1.570	1.155
Vibration 14	0.730	1.566	1.147
Vibration 15	0.740	1.540	1.092
Vibration 16	0.747	1.522	1.056
Vibration 17	0.860	1.240	0.646

**Non-Linear Optical Properties:** NLO properties of a compounds can be predicted with the help of quantum calculations. The relationship between the nonlinear optical properties and the molecular structure can be better understood with the help of Hyperpolarizability. DFT calculations are performed using B3LYP/6-311 G (d, p) to calculate the electronic properties like total dipole moment( $\mu$ ), mean linear polarizability ( $\alpha$ ), anisotropic polarizability ( $\Delta\alpha$ ), first-order hyperpolarizability ( $\beta$ ) and second order hyperpolarizability ( $\gamma$ ). The results obtained by the calculations are shown in table 7. The calculations are carried out according to following equations.

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2) \quad (1)$$

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (2)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2)]^{1/2} \quad (3)$$

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (4)$$

where  $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$  ,  $\beta_y = \beta_{yyy} + \beta_{yxx} + \beta_{yzz}$  and  $\beta_z = \beta_{zzz} + \beta_{zyy} + \beta_{zxx}$

$$\gamma = \frac{1}{5} (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{yzzx}) \quad (5)$$

The conversion factor of  $\alpha$ ,  $\beta$  and  $\gamma$  in atomic unit are

For  $\alpha$  1 atomic unit (a.u.) =  $0.1482 \times 10^{-24}$  electrostatic unit (esu),

For  $\beta$  1 a.u. =  $8.6393 \times 10^{-33}$  esu and

For  $\gamma$  1 a.u. =  $5.0367 \times 10^{-40}$  esu.

Table 7

Dipole moment ( $\mu$ ) In Debye		Mean Linear Polarizability ( $\alpha$ ) in a.u		First-order Hyperpolarizability ( $\beta$ ) in a.u.		Second order Hyperpolarizability ( $\gamma$ ) in a.u	
$\mu_x$	1.4060	$\alpha_{xx}$	-116.6766	$\beta_{xxx}$	23.4687	$\gamma_{xxxx}$	-2677.0804
$\mu_y$	-0.2168	$\alpha_{yy}$	-107.5779	$\beta_{yyy}$	-0.0970	$\gamma_{yyyy}$	-2399.8425
$\mu_z$	0.0000	$\alpha_{zz}$	-108.6294	$\beta_{zzz}$	0.0001	$\gamma_{zzzz}$	-113.6625
Total $\mu$	1.4227	$\alpha_{xy}$	-3.6058	$\beta_{xxy}$	12.0407	$\gamma_{xxyy}$	-72.5421
		$\alpha_{xz}$	-0.0001	$\beta_{xxz}$	24.1535	$\gamma_{xxzz}$	-0.0040
		$\alpha_{yz}$	0.0001	$\beta_{xzz}$	0.0003	$\gamma_{yyyz}$	-33.2559
		$\alpha$	-110.9613 a.u	$\beta_{yzz}$	-2.9258	$\gamma_{yyzz}$	0.0004
			$-16.4444 \times 10^{-24}$ esu	$\beta_{yzz}$	-1.0883	$\gamma_{zzzx}$	-0.0004
		$\Delta\alpha$	10.6411 a.u	$\beta_{yyz}$	-0.0004	$\gamma_{zzzy}$	-0.0001
				$\beta_{yxx}$	-0.0001	$\gamma_{xxyy}$	-900.9610
				$\beta$	40.5737 a.u	$\gamma_{xxzz}$	-471.7032
						$\gamma_{yyzz}$	-439.4798
						$\gamma_{xxyy}$	0.0000
						$\gamma_{yyzz}$	0.0000
						$\gamma_{zzxy}$	7.55182
						$\gamma$	-1762.9746 a.u

**Frontier Molecular Orbitals:** The electronic absorption describes the transition from the ground state to the first excited state and is explained as one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The following figure 5 shows the HOMO and LUMO levels. The HOMO level is at -0.27608 a.u. and LUMO at -0.10925 a.u. and the difference between the two levels is 0.16683 a.u. which indicates a better stability of the compound.

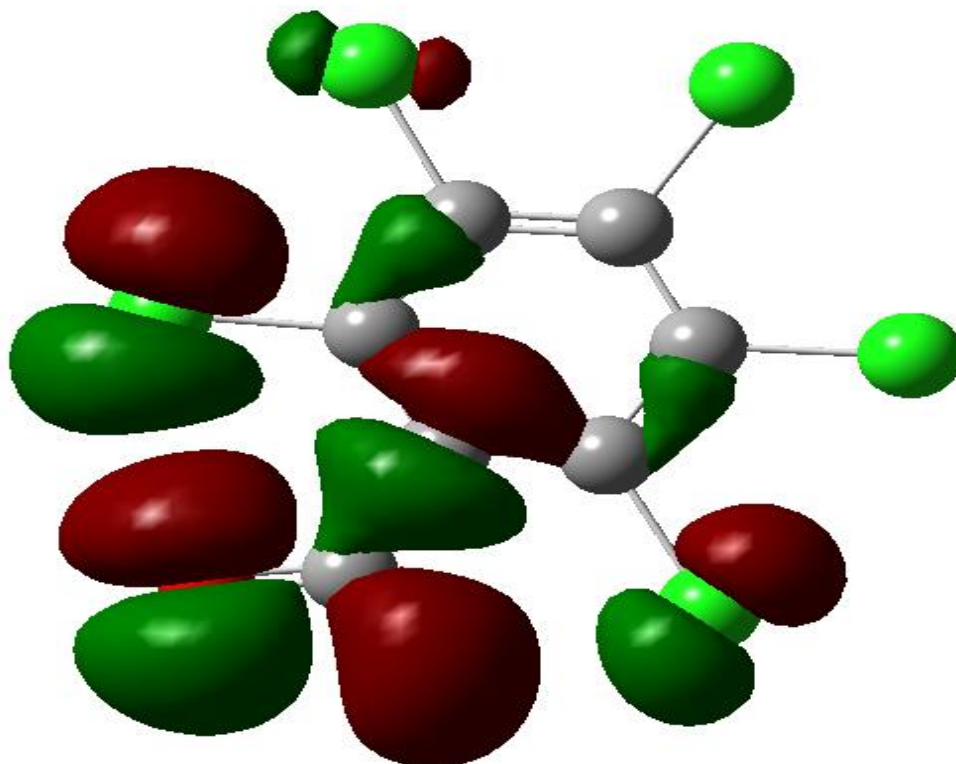


Figure 5

**Molecular Electrostatic Potential:** The molecular electrostatic potential (MESP) is a pictorial representation of electrostatic potential shown on a constant electron density surface and it at the same time exhibits the molecular parameters as shape, size and electrostatic potential value represented in terms of colour coding. The different set of values of the electrostatic potential on the surface can be denoted by different colours as red colour depicts the region of the most electro-negative electrostatic potential, blue the region of the most electro-positive electrostatic potential, green the region of zero potential and yellow slightly electron rich region. This method represents the charge density on a molecule in a glance. In case of our reported compound the molecular electrostatic potential obtained by B3LYP/6-31G(d,p) is shown in figure 6.

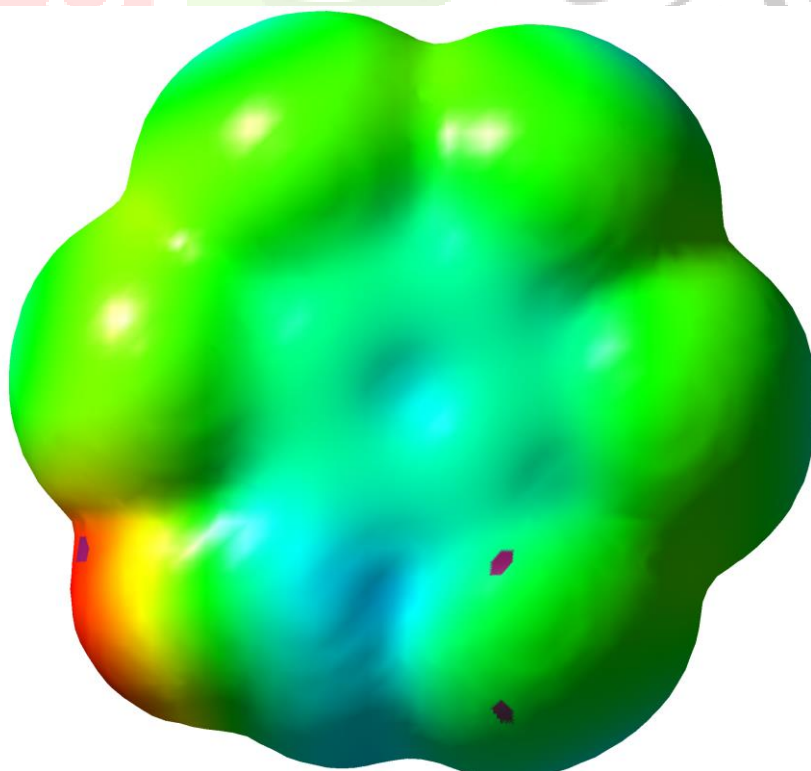


Figure 6



**Conclusion:** In this study an attempt is made to study different properties of the compound pentachloro benzaldehyde which can provide data for further detailed study for various research purposes for applied field.

#### References:

1. A. Nataraj, V. Balachandran, T. Karthick, J. Mol. Struct. 1006 (2011) 104–112.
2. S. Takeuchi, M. Kochi, K. Sakaguchi, K. Nakagawa, T. Mizutani, Agric. Biol. Chem. 42 (1978) 1449.)
3. Takao Itoh, J. Mol. Struct. 786 (1) (2006) 39.
4. T.G. Strand, M.A. Tafipolsky, L.V. Vilkov, H.V. Volden, J. Mol. Struct. 443 (1–3) (1998) 9.
5. E. Bock, E. Tomchuk, Can. J. Chem. 50 (1972) 2890.
6. Peter D.J. Anderson, M. Tereza Fernandez, Gabriella Pocsfalvi, Rod S. Mason, J. Chem. Soc. Perkin Trans. 2 (1997) 873.
7. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
8. R.K. Goel and A.K. Wahid, Indian J. Phys. (1983)57 B, 363
9. B.S.Yadav, Vir Singh, M.K. Yadav and Sanjeev Chaudhry, Indian J. Pure. Appl. Phys. (1997)35,305.
10. Seema, B.S. Yadav, Sachin Kumar, International Journal for Research in Engineering Application & Management (IJREAM) ISSN: 2454-9150 Vol-05, Issue-02, May 2019.

