Vibrational Spectroscopy Investigation using ab Initio and Density Functional Theory Analysis on the Structure of 4-chloro-3-nitrobenzaldehyde

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Abstract—*Benzaldehydes and its derivatives are the simplest in aromatic aldehydes and have wide range of use in different industries, they also exhibits different biological activities. Due to this reason there exist a vast field of study of substituted benzaldehydes. Raman and IR experimental investigations on the 4-chloro-3-nitrobenzaldehyde has been performed and DFT (B3LYP/6-311+G(d,p)) calculations have been performed giving energies, optimized structures, harmonic vibrational frequencies, infrared intensities and Raman activities. The HOMO and LUMO energy gap reveals that the energy gap reflects the chemical activity of the molecule and the molecular electrostatic potential has also been discussed. The observed and calculated wave numbers are found to be in good agreement. The experimental spectra also coincide satisfactorily with those of theoretically constructed spectra.*

Keywords: *4-chloro-3-nitrobenzaldehyde, vibrational spectra, DFT, HOMO and LUMO, molecular electrostatic potential.*

INTRODUCTION

The benzaldehyde and its derivatives have drawn attention and interest of the researchers because of their chemical and biological importance. The benzaldehyde and substituted benzaldehydes have been subjected to various spectroscopic studies [1].The vibrational spectra are very useful for understanding of specific biological activities and for the analysis of relatively complex system. Benzaldehydes have a wide range of usage in different industries as perfumes, flavouring compounds, soaps, foods, preparations of some aniline dyes, solvent for oils etc.[2]. They have also shown anti-tumour activity in mice [2,3].In this light lots of aspects of substituted benzaldehydes and its derivatives are unexplored in spite of the fact that much work has been done on these compounds [4-7].So the IR and Raman spectra obtained experimentally is compared along with assignments with the one obtained from Gaussian 09 W program [8] Molecular structure with bond lengths, bond angles and dihaderal angles is obtained by the software and frontier molecular orbitals and molecular electrostatic potentials are displayed pictorially.

Experimental Spec. pure grade sample of 4-chloro-3-nitrobenzaldehyde (here after referred as 4,3-CNB, M.P 63-65°C) was purchased from M/s Aldrich Chemical Co., U.S.A. and was used as such. Its purity was confirmed by melting point determination. The infrared spectra of the compound 4,3-CNB were recorded on Perkin-Elmer M-683 spectrophotometer in the region 400-4000 cm^{-1} using KBr pellets and nujolmull solvent. The laser Raman spectrum in the region 40-4300 cm^{-1} was recorded on "Spex Rama Lab" spectrophotometer using 52 mg argon-krypton laser beam of wavelength 488 nm.

Computational All the calculations were carried out for 4,3-CNB with Gaussian 09W program package [8]using the Becke-3Lee-Yang-Parr (B3LYP) functional supplemented with the standard 6-311+G(d,p) basis set further referred as DFT calculations. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum, as revealed by the absence of imaginary values in the wave number calculations.

RESULTS AND DISCUSSION

MOLECULAR STRUCTURE: The molecular structure of the mentioned compound 4,3CNB 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 1 isin 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. [9]
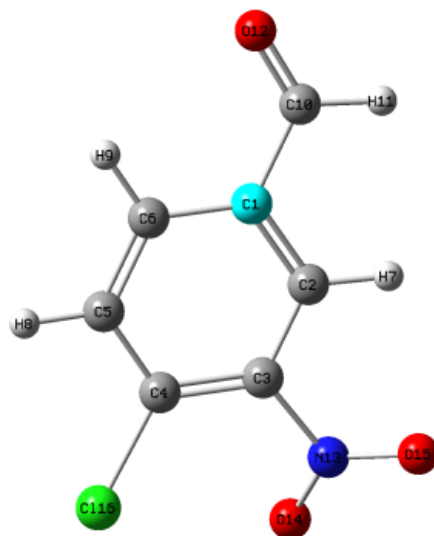
Vibrational Spectroscopy Investigation using ab Initio and Density Functional Theory Analysis on the Structure of 4-chloro-3-nitrobenzaldehyde

261

Figure 1

TABLE 1: Calculated Optimized Geometrical Parameters of4,3CNB, at B3LYP/6-31G(d,p): bond length (Å), bond angle(º), dihedral angles(º)

S. No	Atoms of molecule	Bond length (Å)	Angle between atoms (º)	Bond angle (º)	Dihedral angle between atoms (º)	Dihedral angle (º)
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(2,1,10)	119.9972	D(6,1,2,7)	179.9532
3.	R(1,10)	1.54	A(6,1,10)	120.0043	D(10,1,2,3)	-179.9729
4.	R(2,3)	1.3947	A(1,2,3)	120.0086	D(10,1,2,7)	-0.052
5.	R(2,7)	1.0997	A(1,2,7)	119.9808	D(2,1,6,5)	0.0149
6.	R(3,4)	1.3954	A(3,2,7)	120.0106	D(2,1,6,9)	179.9892
7.	R(3,13)	1.47	A(2,3,4)	119.9942	D(10,1,6,5)	-179.9729
8.	R(4,5)	1.3948	A(2,3,13)	120.0128	D(10,1,6,9)	-0.0056
9.	R(4,16)	1.76	A(4,3,13)	119.993	D(2,1,10,11)	-89.9606
10.	R(5,6)	1.3951	A(3,4,5)	119.994	D(2,1,10,12)	90.0394
11.	R(5,8)	1.0998	A(3,4,16)	119.9811	D(6,1,10,11)	90.0341
12.	R(6,9)	1.0996	A(5,4,16)	120.0249	D(6,1,10,12)	-89.9659
13.	R(10,11)	1.07	A(4,5,6)	120.0047	D(1,2,3,4)	-0.0568
14.	R(10,12)	1.2584	A(4,5,8)	120.0113	D(1,2,3,13)	179.9619
15.	R(13,14)	1.36	A(6,5,8)	119.984	D(7,2,3,4)	-179.9777
16.	R(13,15)	1.36	A(1,6,5)	120.0	D(7,2,3,13)	0.041
17.			A(1,6,9)	120.008	D(2,3,4,5)	0.0341
18.			A(5,6,9)	119.992	D(2,3,4,16)	-179.9964
19.			A(1,10,11)	119.8865	D(13,3,4,5)	-179.9846
20.			A(1,10,12)	120.2269	D(13,3,4,16)	-0.0151
21.			A(11,10,12)	119.8865	D(2,3,13,14)	-123.5746
22.			A(3,13,14)	109.4712	D(2,3,13,15)	116.4254
23.			A(3,13,15)	109.4712	D(4,3,13,14)	56.4441
24.			A(14,13,15)	109.4713	D(4,3,13,15)	-63.5559
25.					D(3,4,5,6)	0.0131
26.					D(3,4,5,8)	-179.9995
27.					D(16,4,5,6)	-179.9563
28.					D(16,4,5,8)	0.0311
29.					D(4,5,6,1)	-0.0376
30.					D(4,5,6,9)	179.9881
31.					D(8,5,6,1)	179.975
32.					D(8,5,6,9)	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 6-311+G(d,p), there is a good agreement between the observed frequencies and those calculated by the DFT, the comparative chart is shown in Table 2 in which experimental values of IR (KBr and nuzol), FTIR and laser Raman are displayed and simultaneously compared with the calculated values.

Table 2

S. No.	Experimental			Calculated	Assignments
	Raman	IR(KBr)	IR(nuzol)		
1.	40				
2.	63			51.47	
3.	146			160.92	
4.		486		497.49	
5.		533		539.65	
6.		613		626.84	
7.	658	656	655	669.21	
8.		724	723		
9.		755	755	738.25	
10.		818	818		
11.	834	831	831	828.50	**CHO deformation of ald. group**
12.		910	910		**C-H out of plane bending**
13.		920		925.73	**C-H out of plane bending**
14.		975	975		**C-H out of plane bending**
15.		1006	1007	998.08	
16.		1051	1050	1066.27	
17.	1213	1202	1201	1230.26	**C-H in plane bending**
18.		1297	1296	1296.32	**C-H in plane bending**
19.	1370	1359	1377	1351.86	**C-H in plane bending**
20.		1412	1412	1415.83	**C-H in plane bending**
21.		1478	1461	1453.31	
22.		1543	1553	1515.41	
23.	1584	1596	1568		
24.	1610	1599	1598		
25.	1679	1638		1640.95	
26.		1702	1700	1666.42	**C=O stretching**
27.		1737	1737		
28.			1814	1806.42	
29.	2750		2728		
30.	2882	2858	2855		**C-H stretching vibrations**
31.			2926	2935.66	
32.	3084	3099			**C-H stretching**
33.	3150			3221.45	
34.		3415	3386	3233.89	
35.			3651		
36.			3678		

Aldehyde Group Vibration In aldehyde group the C–H stretching vibrations usually appear in the region 2871–2806 cm^{-1}[10], in our study the Raman band at 2882 and IR(KBr) at 2858 cm^{-1} and IR(nuzol) at 2855 cm^{-1} lies in this range the calculated value 2935.45 cm^{-1} is close to the experimental value. The carbonyl (C=O) stretching vibrations in the substituted benzaldehydes are reported near 1700 cm^{-1}.[10], the observed IR bands (KBr and nuzol respectively)at 1702 cm^{-1} and 1700 cm^{-1} can be assigned for it and the corresponding calculated value is 1666.42 cm^{-1}. A weak-to-medium intensity band due to aldehyde group CHO deformation vibrationis found in the region 975-780 cm^{-1}[11] the Raman band at 834 cm^{-1} and IR bands at 831 cm^{-1} (for both KBr and nuzol) and the corresponding calculated value 828.50 cm^{-1} is assigned for it

C-H Vibrations The aromatic structure shows C–H stretching vibration in the region 3100–3000 cm^{-1}[12] in our study the Raman band at 3084 cm^{-1} and IR at 3099 cm^{-1} can be assigned to C-H stretching which shows agreement with calculated value 2935.66 cm^{-1}The IR bands at 1478, 1461 cm^{-1}and the Raman bands at 1370 cm^{-1} and 1213 cm^{-1} were assigned to C–H in-plane bending vibration of our compound these values shows good agreement with the calculated values 1230.26, 1296.32, 1351.86, 1415.83 cm^{-1}. The C–H out-of-plane bending vibrations of 4,3-CNB was identified at 834 cm^{-1}in the Raman and 910, 920, 975

Vibrational Spectroscopy Investigation using ab Initio and Density Functional Theory Analysis on the Structure of 4-chloro-3-nitrobenzaldehyde

263

cm^{-1} in the IR spectra are found to be well within their characteristic region and literature [13,14] this is in agreement with the calculated value of 925.73 cm^{-1}

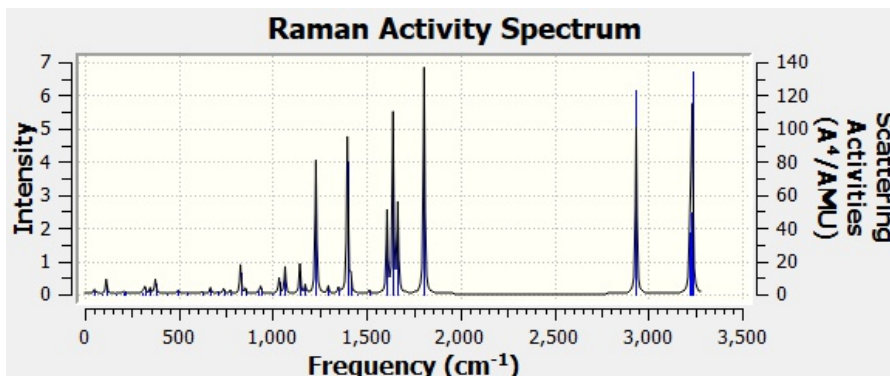Raman and IR spectra obtained by DFT calculations are displayed in figure 2 and figure 3 respectively.
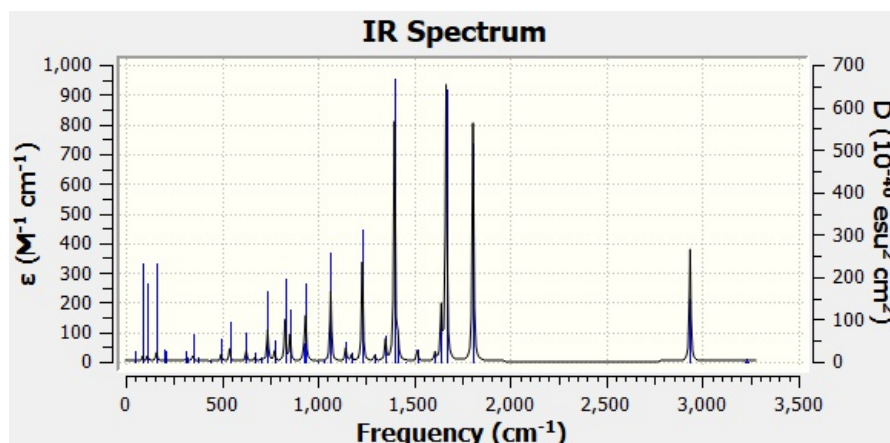

Figure 2

Figure 3

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 figures 2and 3 shows the HOMO and LUMO levels. The HOMO level is at -0.28062 a.u. and LUMO at -0.10682a.u. and the difference between the two levels is 0.1738a.u. which indicates a better stability of the compound.
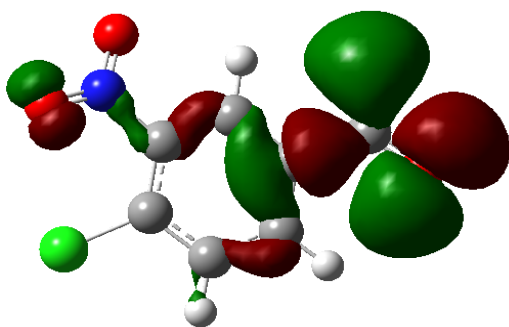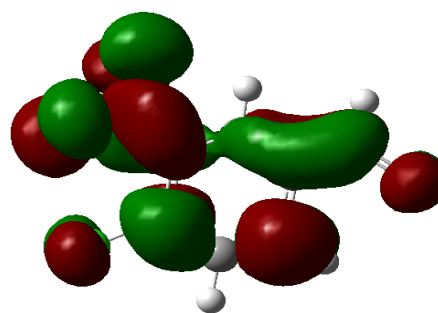

Figure 4

Figure 5

MOLECULAR ELECTROSTATIC POTENTIAL The molecular electro-static 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 electronegative 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/6-311+G(d,p) is shown in figure 6.
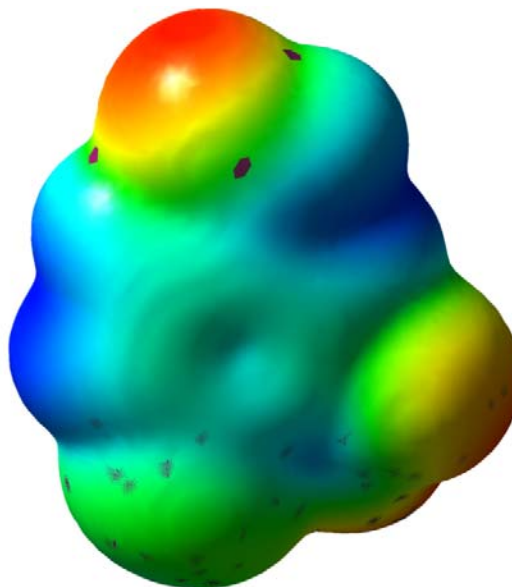

Figure 6

References

[1] C.S. Hiremath, JayashreeYenagi, J. Tonannavar, Spectrochim. Acta Part A 68 (2007) 710–717.
[2] A. Nataraj, V. Balachandran, T. Karthick, J. Mol. Struct. 1006 (2011) 104–112.
[3] S. Takeuchi, M. Kochi, K. Sakaguchi, K. Nakagawa, T. Mizutani, Agric. Biol. Chem. 42 (1978) 1449.)
[4] Takao Itoh, J. Mol. Struct. 786 (1) (2006) 39.
[5] T.G. Strand, M.A. Tafipolsky, L.V. Vilkov, H.V. Volden, J. Mol. Struct. 443 (1–3) (1998) 9.
[6] E. Bock, E. Tomchuk, Can. J. Chem. 50 (1972) 2890.
[7] Peter D.J. Anderson, M. Tereza Fernandez, Gabriella Pocsfalvi, Rod S. Mason, J. Chem. Soc. Perkin   Trans. 2 (1997) 873.
[8] 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.
[9] Kennedy, Alan R et al.Section E, Structure reports online vol. 66, 2010,
[10] V. Krishnakumar, R. John Xavier, Indian J. Pure Appl. Phys. 41 (2003) 95–99.
[11] G. Eazhilarasi, R. Nagalakshmi, V. Krishnakumar, Spectrochim. Acta 71A (2008) 502–507.
[12] J. Mohan, Organic Spectroscopy—Principles and Applications, 2nd ed., Narosa Publishing House, New Delhi, 2001.
[13] S. Jeyavijayan, M. Arivazhagan, Indian J. Pure Appl. Phys. 48 (2010) 869–874.
[14] P. Anbarasu, M. Arivazhagan, Indian J. Pure Appl. Phys. 49 (2011) 227–233.