

COMPUTATIONAL STUDIES ON STRUCTURE AND VIBRATIONAL SPECTRA OF O-CHLOROPHENOL AND TETRAHYDROFURAN

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ABSTRACT

The molecular structure and vibrational spectra of o-Chlorophenol and tetrahydrofuran have been investigated by Hartree-Fock (HF) and Density Functional Theory (DFT) using standard B3LYP functional and 6-31G (d,p) basis set. The results of the calculations are applied to simulate infrared spectra of the title compounds which showed good agreement with the experimentally determined data. It has been found that both methods yield consistent data for the geometric parameters but DFT yielded vibrational frequencies much closer to the experimental data. Computed values at DFT (B3LYP)/6-31G (d,p) have analyzed and their characterization was made with help of Gauss view visualization program utilizing the data obtained from the Gaussian 03 calculation. A few of the discrepancies observed between the experimental and computed data of vibrational frequencies and their assignments have also been discussed.

Keywords: Infrared spectra, o-Chlorophenol, Ethers, Normal mode frequencies.

INTRODUCTION

The most frequently spectroscopic methods for organic chemists are Ultra-Violet, Infra-Red, Nuclear Magnetic Resonance and Mass-Spectrometry. I.R. measurement through liquid mixtures provide an excellent tool to investigate inter and intramolecular interactions between like and unlike molecules.

Recently, a spectroscopic study of o-Chlorophenol and tetrahydrofuran has been made and its various vibrational modes have been assigned using simplified picture of the molecule. Due to existence of many vibrations, it would be difficult to assign the observed frequencies to a particular mode. The density functional theory¹ (DFT) methods have become a powerful tool for the investigation of molecular structure and vibrational spectra. Supplemented by a visualization program, the

assignments can accurately be made. The present work has been performed with view point of getting the vibrational frequencies on an optimized geometry of the titled compound. These frequencies are analyzed and compared with the experimental data². Attempts have been made to find out an optimum method using a basis set to get a close agreement between the computed and the experimental data. Literature survey shows that no computational studies have been done so far on the titled compound.

This program reports energy, dipole moment, charges, vibrational frequencies, bond angle and bond distance. It is also useful tool for calculations on larger and runs calculations very quickly.

EXPRIMENTAL DETAILS

FTIR spectra were recorded on a FTIR spectrometer (Model: SIMADZU 8400S PC) by using KBr pellet in the region 400-4000 cm^{-1} with 4.0 cm^{-1} resolution. The transmission values were read in steps of 5%. The spectrometer possesses out to aligned energy optimization and dynamically aligned interferometer. It is fitted with KBr beam splitter, a DLATGS detector. A base line correction was made for the spectra recorded.

Fig 1 represents the infrared spectra of o-Chlorophenol; we notice the broad and sharp band of O-H stretching at 3621 cm^{-1} , the weak band of aromatic C-H appears at 3078 cm^{-1} . The two C=C stretching at both 1480 cm^{-1} and 1595 cm^{-1} are observed. The stretching frequency of C-O and C-Cl are noted at 1190 cm^{-1} and 748 cm^{-1} respectively.

Fig 2 shows the infrared spectra of tetrahydrofuran, the two sharp and strong bands are observed at frequencies 2865 cm^{-1} and 2975 cm^{-1} corresponding to C-H vibration. A band at 1070 cm^{-1} is assigned as C-O stretching vibration.

COMPUTATIONAL DETAILS

Geometry optimization and vibrational frequencies of titled compounds were calculated at the Hartree-Fock³ and DFT levels with B3LYP (Becke-Lee-Yang-Parr three parameters) hybrid functional⁴ with correlation function such as one proposed by Lee, Yang and Parr⁵. B3LYP is most promising in providing reasonable acceptable vibrational wave numbers for organic molecules. Standard 6-311G (d,p) basis set have been used in the both methods in order to see the effect of correlation. Gaussian 03 software package⁶ have been utilized to accomplish all the calculations.

RESULT AND DISUSSION

All the theoretical calculations of o-Chlorophenol and Tetrahydrofuran were performed by the use of G03W series of programs. Geometries of optimizations for all of the investigated molecules in this work were carried out using the HF and DFT (B3LYP) method with 6-31G (d, p) basis sets. Computed geometrical parameters are listed in Table 1. Results show that both levels predict consistent data. An optimized geometry of titled compounds at DFT (B3LYP)/6-31G (d, p) level is shown in Fig. 3. The detailed analysis of the vibrational frequencies has been performed with computed data obtained at HF and DFT (B3LYP)/6-31G (d, p) and results are

presented in Table 2. The intensities are calculated from the computed data and these are also listed in Table 2.

The computed values have been utilized to simulate IR spectra. The result shows an agreement with the experimentally observed spectra of titled compounds. A comparison of observed spectra and computational data reveals the agreement. During the present study, visualization of frequencies in 3D has been made by Gassview. With this program, assignments of vibrations can made with high degree of certainty. Accepted values of scaling factors for DFT is 0.96 and it has been used to correct the frequency values⁷. Scaled frequencies are recorded in Table 2. The assignment of the computed frequencies is done by visualizing the vibrations in 3D using Gausview (Table 2). The values of IR frequencies are compared and the discrepancies observed between experimental and computational data are discussed here.

O-H vibrations

o-Chlorophenol

The non hydrogen-bonded hydroxyl group of phenols absorbs strongly in the 3584-3700 cm^{-1} region. In the present investigation, the calculations show O-H stretching vibrations at 3611.45 cm^{-1} and these are close agreement with the experimental values of 3621 cm^{-1} . The OH bending in plane is found at 1573.96, 1442.39 and 1326.93 cm^{-1} . Visualization of these vibrations shows that these are contaminated by β (CH) and ν (C=C). The wagging of OH is observed at 1004.93 and 475.99 cm^{-1} along with ring deformation.

C-H vibrations

o-Chlorophenol

In aromatic compound, C-H stretching vibrations⁸ occur in the region 3000-3100 cm^{-1} , which is the characteristics region for the ready identification of C-H stretching vibrations^{9,10}. The calculation shows four C-H stretching vibrations at 3093.30, 3087.98, 3078.47 and 3065.36 cm^{-1} and these are in close agreement with the experimental value 3078 and 3040 cm^{-1} . The C-H in plane bending vibrations are visualized at 1588.95, 1573.96, 1465.81, 1442.39, 1326.93, 1289.09, 1238.07, 1136.49, 1100.83 and 1022.80 cm^{-1} . Visualization of these frequencies reveals that these vibrations are contaminated by ring deformation, O-H bending, C-C and C-O stretching. The computed values for the C-H wagging are at 939.04, 902.04 and 825.05 cm^{-1} . The experimental values are at 933 and 833 cm^{-1} .

Tetrahydrofuran

The molecular structure shows the presence of C-H stretching vibrations in the region 2800-3000 cm^{-1} . In the present study, the C-H vibrations have been found 2975, 2865 cm^{-1} by experimental and computed values are 3001.41, 2981.19, 2958.35, 2887.69 cm^{-1} .

Scissoring of C-H occurs at 1500.76, 1485.38, 1467.46, 1447.88 and 1234.88 cm^{-1} . Rocking and twisting observed at 1363.54, 1323.08, 1272.28, 1155.00, 1121.26 cm^{-1} and 1223.49, 1205.11, 1204.37 cm^{-1} .

C=C vibrations

o-Chlorophenol

The C=C stretching vibrations occur in the region 1400 - 1680 cm^{-1} . Therefore, in the present study the C=C stretching vibrations of the titled compound is observed at 1465.81 and 1442.39 cm^{-1} along with the plane bending due to $\beta(\text{CH})$ and $\beta(\text{OH})$ while the experimental value is at 1480 and 1460 cm^{-1} . The calculated frequencies are on lower side as compared to the experimental values. This may be due to contamination with other coupled vibrations¹¹. Computationally, the C=C out of plane bending is found at 528.60 cm^{-1} .

C-O vibrations

o-Chlorophenol

The band due to C-O-C stretching vibrations is observed in the region 1000-1300 cm^{-1} . These vibrations are found at 1289.09, 1238.07 and 1171.04 cm^{-1} along with bending due to $\beta(\text{CH})$ and $\omega(\text{OH})$. Experimental values are observed at 1199 and 1185 cm^{-1} .

Tetrahydrofuran:- The computational results listed in Table 4 show that C-O stretching are found at 1101.88 and 1026.58 cm^{-1} . The experimental observed value of C-O stretching is found at 1184 and 1070 cm^{-1} . Ring

deformation is computationally assigned at 867.44 and 691.32 cm^{-1} .

C-Cl vibrations

o-Chlorophenol

The C-Cl stretching frequency is generally observed in the region 800-600 cm^{-1} depending on the configuration and conformation of the compound¹². Based on this, in the present investigation C-Cl stretching mode vibrations has been assigned to 658.23 cm^{-1} along with ring deformation, while the FTIR band identify at 748 cm^{-1} . The $\nu(\text{OH-Cl})$ is also observed at 360.87 and 243.04 cm^{-1} presented in Table 2.

CONCLUSION

The normal mode frequencies and corresponding vibrational assignment of titled compound are examined theoretically using the Gaussian 03 package. The optimized geometries and complete vibrational analysis of o-Chlorophenol and Tetrahydrofuran were performed and analyzed both at HF and DFT levels of theories utilizing 6-31 G(d,p) basis set. The data obtained during the course of present investigation show that a better agreement between the experimental and computed data is obtained by using DFT method. HF method shows disagreement with experimental data. Some of the assignments made contradictory to the computed data. However, the assignments made during the present investigation can put a greater confidence level because these are visualized in three dimensions using a Gaussview program.

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Table 1: Optimized geometrical parameters of o-Chlorophenol and Tetrahydrofuran obtained by HF and DFT calculation

Parameter	HF 6-31 G (d,p)	DFT 6-31 G (d,p)	Parameter	HF 6-31 G (d,p)	DFT 6-31 G (d,p)
Bond length (Å)	o-Chlorophenol		Bond length (Å)	Tetrahydrofuran	
C1-C2	1.385	1.392	C1-O2	1.403	1.424
C2-C3	1.388	1.403	O2-C3	1.403	1.424
C3-C4	1.390	1.400	C3-C4	1.538	1.545
C4-C5	1.179	1.391	C4-C5	1.541	1.547
C5-C6	1.388	1.397	C5-C1	1.538	1.545
C1-C6	1.381	1.394	C1-H6	1.086	1.098
C1-H7	1.074	1.084	C1-H7	1.086	1.098
C2-Cl13	1.750	1.767	C3-H8	1.086	1.098

C3-O11	1.341	1.356	C3-H9	1.086	1.098
C4-H8	1.074	1.085	C4-H10	1.084	1.093
C5-H9	1.075	1.086	C4-H11	1.084	1.093
C6-H10	1.074	1.085	C5-H12	1.084	1.093
O11-H12	0.944	0.970	C5-H13	1.084	1.093
Bond Angle(degree)			Bond Angle (degree)		
C1-C2-C3	121.17	121.52	C1-O2-C3	113.39	112.19
C3-C4-C5	120.37	120.40	O2-C1-C5	108.14	108.58
C4-C5-C6	120.66	120.63	O2-C3-C4	108.14	108.58
C5-C6-C1	119.37	119.64	C1-C5-C4	105.17	105.32
C1-C2-C113	119.56	120.16	C5-C4-C3	105.17	105.32
C3-O11-H12	111.41	108.80	H6-C1-H7	107.63	107.32
C2-C1-H7	119.21	119.38	H8-C3-H9	103.63	107.32
C1-C6-H10	119.96	119.75	H10-C4-H11	107.05	106.93
C5-C6-H10	120.68	120.62	H12-C5-H13	107.05	106.93
C4-C5-H9	119.33	119.34			
C5-C4-H8	121.54	121.63			
C3-C4-H8	118.09	117.97			
C4-C3-O11	117.78	118.30			

Table 1 conti.

Parameter	HF 6-31 G (d,p)	DFT 6-31 G (d,p)	Parameter	HF 6-31 G (d,p)	DFT 6-31 G (d,p)
Energy (a.u.)	o-Chlorophenol		Energy (a.u.)	Tetrahydrofuran	
	-764.4727	-767.0747		-230.9833	-232.3713
Dipole mom. (debye)	1.2485	0.9114	Dipole mom. (debye)	1.9474	2.2377

Table 2: Fundamental Vibrations of o-Chlorophenol calculated at DFT/B3LYP 6-31 G(d, p)

Normal Mode	Calculated Frequencies (cm-1) (Scaled)	Intensity	Assignments
1	3611.45 (3621)	73.96	v(OH)
2	3093.30	5.48	vsym(CH)
3	3087.98	7.38	vasym (CH)
4	3078.47 (3078)	9.05	vsym (CH)
5	3065.36 (3040)	2.79	vsym (CH)
6	1588.95	33.47	β (CH) + Ring deformation
7	1573.96	16.89	β (OH) + β (CH)
8	1465.81(1480)	129.51	β (CH) + v (C=C)
9	1442.39 (1460)	5.16	β (OH) + β (CH) + v (C=C)
10	1326.93	28.50	β (OH) + β (CH)
11	1289.09	24.59	β (CH) + v(CO)
12	1238.07 (1199)	73.54	β (CH) + v(CO)
13	1171.04 (1185)	120.28	ω (OH) + v(CO)
14	1136.49	2.05	β (CH)
15	1100.83	4.62	β (CH) + v(CC)
16	1022.80 (1029)	8.47	β (CH) + Ring deformation
17	1004.93	44.37	ω (OH) + Ring deformation
18	939.04 (933)	0.030	ω (CH)
19	902.04	2.48	ω (CH)
20	825.05 (833)	1.38	ω (CH)
21	813.01	10.90	Ring deformation
22	732.67	52.20	ω (CH)
23	680.16	0.25	ω (CH)
24	658.23 (748)	24.32	v(CCl) + Ring deformation
25	531.65	3.91	Ring deformation

26	528.60	0.20	$\gamma(\text{C}=\text{C}) + \gamma(\text{CH})$
27	475.99	11.69	$\omega(\text{OH})$
28	430.56	0.02	$\gamma(\text{Ring})$
29	396.66	116.82	$\omega(\text{OH})$
30	360.87	2.20	$s(\text{OH-Cl})$
31	255.38	0.48	$\gamma(\text{Ring})$
32	243.04	2.82	$s(\text{OH-Cl})$
33	153.55	0.15	$\gamma(\text{Ring})$

Table 3: Fundamental Vibrations of o-Chlorophenol calculated at HF/B3LYP 6-31 G(d, p)

Normal Mode	Calculated Frequencies (cm-1) (Scaled)	Intensity	Assignments
1	4005.22 (3621)	112.89	$\nu(\text{OH})$
2	3251.44	7.67	$\nu_{\text{sym}}(\text{CH})$
3	3246.40	10.33	$\nu_{\text{asym}}(\text{CH})$
4	3234.39 (3078)	11.09	$\nu_{\text{asym}}(\text{CH})$
5	3218.80 (3040)	3.53	$\nu_{\text{asym}}(\text{CH})$
6	1729.52	26.77	$\nu(\text{C}=\text{C}) + s(\text{CH})$
7	1714.85	42.48	$\nu(\text{C}=\text{C}) + s(\text{CH})$
8	1592.04	159.14	$\rho(\text{CH}) + \nu(\text{C}=\text{C})$
9	1557.00	8.55	$\rho(\text{CH})$
10	1406.76	12.18	$\rho(\text{CH})$
11	1356.72	148.25	$\nu(\text{CO}) + \omega(\text{OH}) +$
12	1294.40	28.36	$\rho(\text{CH}) + \omega(\text{OH})$
13	1243.81	53.75	$s(\text{CH})$
14	1185.88	6.70	$s(\text{CH}) + \text{Ring deformation}$
15	1152.66	54.52	$s(\text{CH}) + \text{Ring deformation}$
16	1108.00	18.68	$\rho(\text{CH}) + \text{Ring deformation}$
17	1079.53	30.13	$\rho(\text{CH}) + \text{Ring deformation}$
18	1066.26	0.36	$\omega(\text{CH})$
19	1031.85 (1029)	3.31	$\omega(\text{CH})$
20	930.66 (933)	3.51	$\omega(\text{CH})$
21	872.45 (833)	12.67	Ring deformation
22	817.2	76.35	$\omega(\text{CH})$
23	764.59	1.74	$\omega(\text{Ring})$
24	709.47 (748)	27.29	$\nu(\text{C-Cl}) + \text{Ring deformation}$
25	583.68	4.35	Ring deformation
26	576.88	0.19	$t(\text{Ring})$
27	515.55	11.89	$\omega(\text{OH})$
28	477.88	1.68	$\omega(\text{Ring})$
29	390.77	2.09	$\omega(\text{Ring})$
30	350.08	146.96	$\omega(\text{OH})$
31	281.48	0.50	$t(\text{Ring})$
32	264.29	2.25	$s(\text{OH-Cl})$
33	167.75	0.38	$t(\text{Ring})$

Table 4: Fundamental Vibrations of Tetrahydrofuran calculated at DFT/B3LYP 6-31 G(d, p)

Normal Mode	Calculated Frequencies (cm-1) (Scaled)	Intensity	Assignments
1	3001.41	60.31	vsym (CH)
2	2981.19 (2975)	0.00	vasym (CH)
3	2958.35	29.77	vsym (CH)
4	2947.65	32.53	vasym (CH)
5	2917.33	94.52	vasym (CH)
6	2915.41	0.00	vasym (CH)
7	2897.43	23.28	vsym (CH)
8	2887.69 (2865)	147.51	vsym (CH)
9	1500.76	0.11	s(CH)
10	1485.38	4.27	s(CH)
11	1467.46	1.45	s(CH)
12	1447.88	0.95	s(CH)
13	1363.54	7.96	ρ (CH)
14	1323.08	0.034	ρ (CH)
15	1272.28	1.13	ρ (CH)
16	1234.88	3.34	s(CH)
17	1223.49	0.00	t(CH)
18	1205.11	1.14	t(CH)
19	1204.37	0.00	t(CH)
20	1155.00	0.19	ρ (CH)
21	1121.26	0.00	ρ (CH)
22	1101.88 (1184)	149.26	v(CO)
23	1026.58 (1070)	8.90	v(CO)
24	637.09	2.36	ρ (CH)
25	919.52	7.13	s(CH) +Ring deformation
26	904.10	23.97	ρ (CH) + v(CO)
27	867.44	0.22	Ring deformation
28	802.59	0.00	ρ (CH)
29	738.03	0.69	ρ (CH)
30	691.32	6.60	Ring deformation
31	681.93	1.66	ω (Ring)

Table 5: Fundamental Vibrations of Tetrahydrofuran calculated HF/B3LYP 6-31 G(d, p)

Normal Mode	Calculated Frequencies (cm-1) (Scaled)	Intensity	Assignments
1	3140.52	112.89	vsym (CH)
2	3118.8	0.00	vasym (CH)
3	3100.64	26.94	vsym (CH)
4	3089.88	79.32	vasym (CH)
5	3085.28	0.003	vasym (CH)
6	3084.45	73.04	vasym (CH)
7	3064.46(2975)	50.56	vsym (CH)
8	3056.91 (2865)	122.50	vsym (CH)
9	1620.06	0.42	s(CH)
10	1605.95	3.66	s(CH)
11	1581.93	1.76	s(CH)
12	1559.82	1.00	s(CH)
13	1494.08	11.19	ρ (CH)
14	1445.50	0.02	ρ (CH)
15	1397.13	0.67	ρ (CH)
16	1361.38	5.43	s(CH)
17	1328.78	0.00	ρ (CH)
18	1318.77	0.76	ω (CH)
19	1310.67	0.00	ω (CH)
20	1266.85	2.05	ω (CH)
21	1241.00 (1184)	193.54	v(CO)
22	1222.31	1.00	ω (CH)
23	1107.53	13.71	v(CC)
24	1009.21	3.86	ω (CH)

25	991.53 (1070)	26.72	v(CO)
26	984.18	8.18	s(CH) + Ring deformation
27	923.51	0.05	Ring deformation
28	862.18	0.00	ρ (CH)
29	786.06	0.13	ρ (CH)
30	774.29	9.55	Ring deformation
31	740.18	1.24	ω (Ring)

Values in bracket refer to the experimental data, v-stretching, v_{sym} -symmetrical stretching, v_{asym} -asymmetrical stretching, β -bending, ω -wagging, ρ -rocking, t- twisting

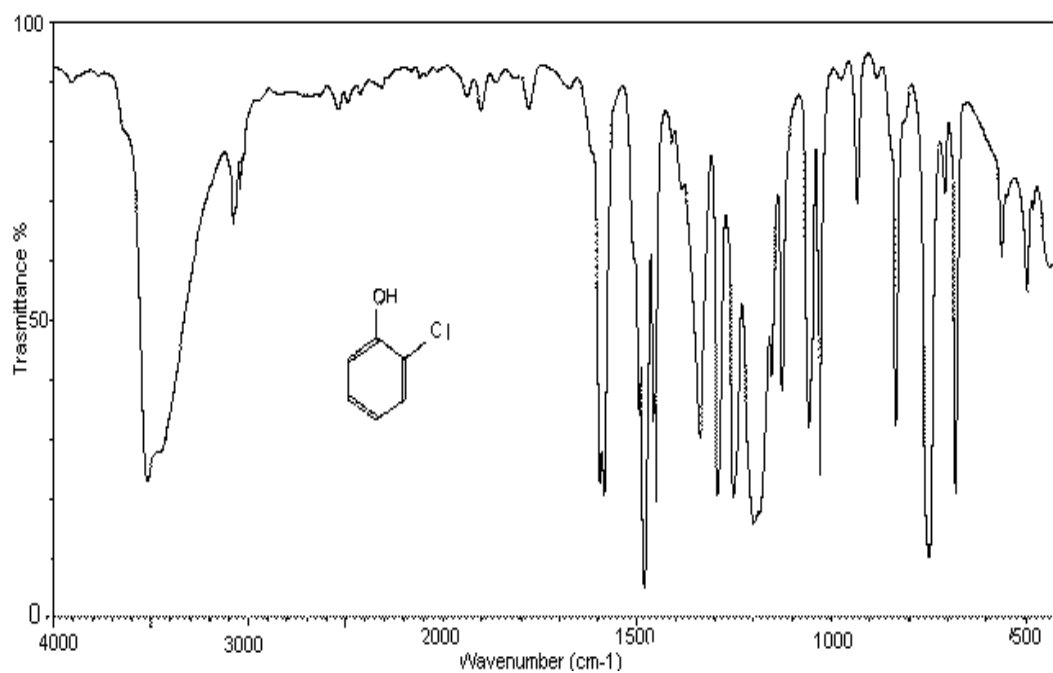


Fig. 1: FTIR Spectra of o-Chlorophenol

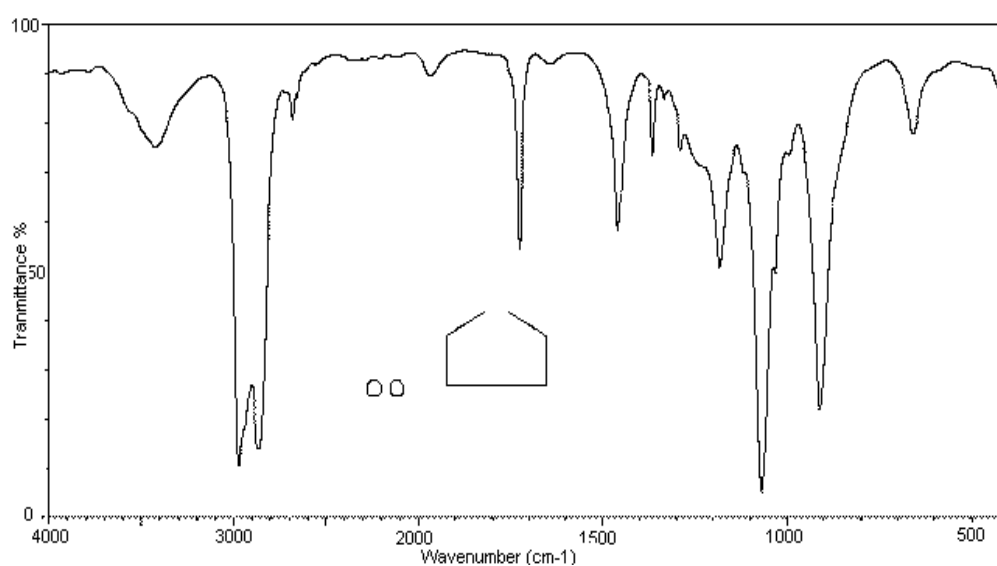


Fig. 2: FTIR Spectra of Tetrahydrofuran

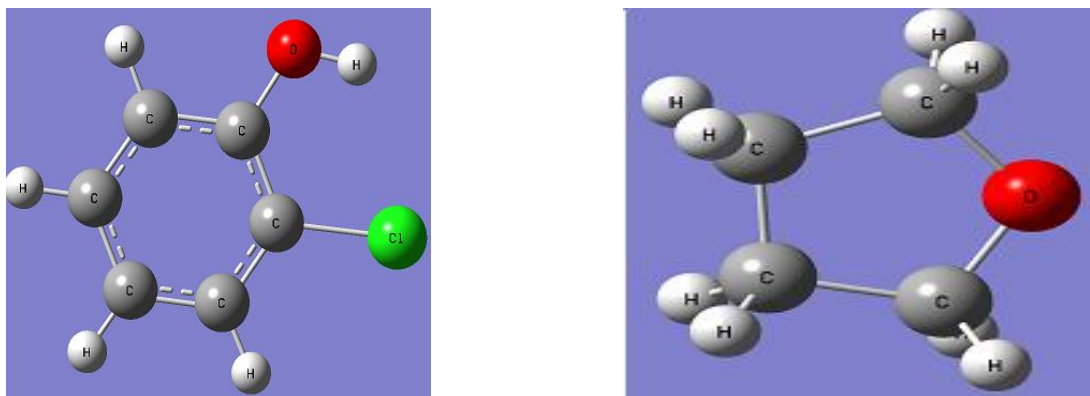


Fig. 3: Optimized geometry of o-Chlorophenol and Tetrahydrofuran obtained at DFT (B3LYP)/6-31G(d, p)

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