

## Quantum chemical study of 4-chloro-3-ethylphenol

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5 Phenol, also known as carboic acid, is an aromatic organic compound with the molecular formula  $C_6H_5OH$ . It is a white crystalline solid that is volatile. The molecule consists of a phenyl group ( $-C_6H_5$ ) bonded to a hydroxyl group ( $-OH$ ). Phenol and its chemical derivatives are key for building polycarbonates, epoxies, Bakelite, nylon, detergents, herbicides such as phenoxy herbicides, and numerous pharmaceutical drugs. So we have done a vibrational spectroscopic investigation on 4-Chloro-3-ethylphenol which is a derivative of phenol. The optimized geometry of the 4-chloro-3-ethylphenol molecule has been determined by DFT/B3LYP with 6-311 G (d, p) as the basis set. Using this optimized structure, we have calculated the infrared wave numbers, which are very useful in absence of experimental data. On based on these results, we have discussed the correlation between the vibrational modes of 4-chloro-3-ethylphenol.

### 15 Introduction

Phenol, also known as carboic acid, is an aromatic organic compound with the molecular formula  $C_6H_5OH$ . It is a white crystalline solid that is volatile. The molecule consists of a phenyl group ( $-C_6H_5$ ) bonded to a hydroxyl group ( $-OH$ ). It is mildly acidic, but requires careful handling due to its propensity to cause burns. Phenol was first extracted from coal tar, but today is produced on a large scale (about 7 billion kg/year) from petroleum. It is an important industrial commodity as a precursor to many materials and useful compounds. Its major uses involve its conversion to plastics or related materials. Phenol and its chemical derivatives are key for building polycarbonates, epoxies, Bakelite, nylon, detergents, herbicides such as phenoxy herbicides, and numerous pharmaceutical drugs. The major uses of phenol, consuming two thirds of its production, involve its conversion to precursors to plastics. Condensation with acetone gives bisphenol-A, a key precursor to polycarbonates and epoxide resins. Condensation of phenol, alkylphenols, or diphenols with formaldehyde gives phenolic resins, a famous example of which is Bakelite. Partial hydrogenation of phenol gives cyclohexanone, a precursor to nylon. Nonionic detergents are produced by alkylation of phenol to give the alkylphenols, e.g., nonylphenol, which are then subjected to ethoxylation. Phenol is also a versatile precursor to a large collection of drugs, most notably aspirin but also many herbicides and pharmaceutical drugs. Phenol is also used as an oral anesthetic/analgesic in products such as Chloraseptic or other brand name and generic equivalents, commonly used to temporarily treat pharyngitis [1]. As a part of our ongoing research work [2-5], here, the main objective of the present study is to investigate in detail the vibrational spectra of the important industrial and biological molecule i.e. 4-Chloro-3-ethylphenol, a derivative of phenol.

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### Computational details

All the calculations were performed by the B3LYP [6, 7] method using the 6-311 G (d, p) basis set of Density functional theory [8]. All computations were carried out with the GAUSSIAN 09 package [9]. By combining the results of the GAUSSVIEW'S program [10] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. Vibrational frequencies for these molecules were calculated with these methods and then scaled [11] by 0.9613.

### Results and Discussion

The optimized Structure parameters of 4-Chloro-3-ethylphenol calculated by B3LYP method using the 6-311 G (d, p) are listed in Table 1 and are in accordance with the atom numbering scheme as shown in Figure 1. After geometry optimization local minimum energy obtained for structured optimization of 4-Chloro-3-ethylphenol is approximately -0.06600900 (a.u.). The calculated optimized bond parameters of molecule are listed in Table 1.

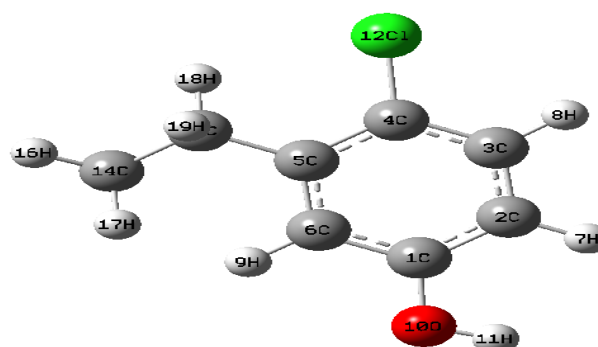


Fig. 1 Model molecular structure of 4-Chloro-3-ethylphenol

In calculated data, the (C-C) bond length varies between the values 1.393 Å- 1.513 Å, while (C-O) bond length varies between 1.367 Å- 1.495 Å which is in good agreement with experimental data i.e. 1.380 Å- 1.535 Å and 1.375 Å- 1.535 Å respectively. (C-H) bond length varies between 1.095 Å- 1.109 Å while (C-Cl) bond length is 1.690 Å in title molecule which is in good agreement with experimental data. (O-H) bond length is 0.9491 Å in title molecule which is 0.8098 Å in experimental data. The (C-C-C) bond angle varies from 118.90-121.14 while (C-C-O) varies between 116.01-123.01-. The (C-C-H) bond angle varies between 119.55-120.20. All the calculated bond angles are also in good agreement with experimental data as given in Table 1.

**Table 1** Bond Length (Å) and Bond Angle of 4-chloro-3-ethylphenol

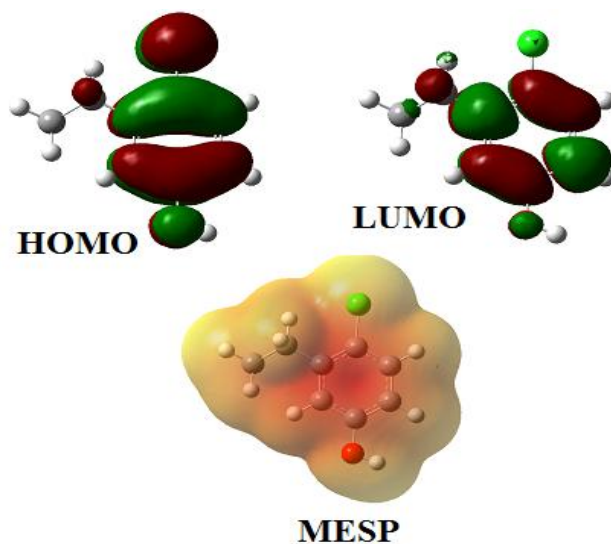
s.no.	Parameter	Experimental value	Calculated value
Bond length			
1.	C <sub>1</sub> -C <sub>2</sub>	1.3880	1.4021
2.	C <sub>1</sub> -C <sub>6</sub>	1.3910	1.3995
3.	C <sub>1</sub> -O <sub>10</sub>	1.3751	1.3678
4.	C <sub>2</sub> -C <sub>3</sub>	1.3850	1.3874
5.	C <sub>2</sub> -H <sub>7</sub>	0.9500	1.0958
6.	C <sub>3</sub> -C <sub>4</sub>	1.3880	1.3932
7.	C <sub>3</sub> -H <sub>8</sub>	0.9500	1.0958
8.	C <sub>4</sub> -C <sub>5</sub>	1.3993	1.3998
9.	C <sub>4</sub> -Cl <sub>12</sub>	1.7430	1.6906
10.	C <sub>5</sub> -C <sub>6</sub>	1.3950	1.3942
11.	C <sub>5</sub> -O <sub>13</sub>	1.5072	1.4953
12.	C <sub>6</sub> -H <sub>9</sub>	0.9500	1.1022
13.	O <sub>10</sub> -H <sub>11</sub>	0.8098	0.9491
14.	C <sub>13</sub> -C <sub>14</sub>	1.5350	1.5135
15.	C <sub>13</sub> -H <sub>18</sub>	0.9900	1.1096
16.	C <sub>13</sub> -H <sub>19</sub>	0.9900	1.1092
17.	C <sub>14</sub> -H <sub>15</sub>	0.9800	1.0975
18.	C <sub>14</sub> -H <sub>16</sub>	0.9800	1.0967
19.	C <sub>14</sub> -H <sub>17</sub>	0.9800	1.1030
Bond angle			
20.	A(2,1,6)	120.5102	120.9736
21.	A(2,1,10)	122.9155	123.0155
22.	A(6,1,10)	116.0009	116.0109
23.	A(1,2,3)	119.1043	118.9073
24.	A(1,2,7)	121.2601	121.1006
25.	A(3,2,7)	118.9623	119.992
26.	A(2,3,4)	120.1234	120.2395
27.	A(2,3,8)	119.8956	120.2075
28.	A(4,3,8)	118.6523	119.5529
29.	A(3,4,5)	120.5624	121.1493
30.	A(3,4,12)	116.9998	117.9391
31.	A(5,4,12)	120.8145	120.9115
32.	A(4,5,6)	119.6524	118.8342
33.	A(4,5,13)	121.0562	121.0649
34.	A(6,5,13)	119.9856	120.0826
35.	A(1,6,5)	119.7825	119.8958
36.	A(1,6,9)	120.3654	121.1297
37.	A(5,6,9)	118.6895	118.9721
38.	A(1,10,11)	106.5562	107.8879
39.	A(5,13,14)	112.3456	113.366
40.	A(5,13,18)	111.2354	110.047
41.	A(5,13,19)	107.5562	107.6138
42.	A(14,13,18)	109.5236	109.6653
43.	A(14,13,19)	110.2564	110.1819

44.	A(18,13,19)	104.2556	105.6665
45.	A(13,14,15)	111.2563	111.6839
46.	A(13,14,16)	112.6598	111.1721
47.	A(13,14,17)	112.3587	111.2273
48.	A(15,14,16)	107.6524	107.578
49.	A(15,14,17)	106.9856	107.1044
50.	A(16,14,17)	108.8954	107.8696

### 15 Electronic Properties, Atomic charge, and Thermodynamic properties

The interaction with other species in a chemical system is also determined by frontier orbitals, HOMO and LUMO. It can also be determined by experimental data. The frontier orbital gap helps to distinguish the chemical reactivity and kinetic stability of the molecule. A molecule which has a larger orbital gap is more polarized having reactive part as far as reaction is concerned [12]. The frontier orbital gap and Dipole moment ( $\mu$ ) is 9.21 eV and 1.0071 Debye for 4-Chloro-3-ethylphenol given in Table 2. The contour plots of the HOMO, LUMO and MESP of the molecule are shown in Figure 2. The importance of MESP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative, and neutral electrostatic potential region in terms of grading and is very useful in the investigation of molecular structure with its physiochemical property relationship [13-15].

The Mulliken atomic charges for all the atoms of the 4-Chloro-3-ethylphenol are calculated by PM3 method in gas phase and are presented in Table 3. Several calculated thermodynamic properties based on the vibrational analysis at B3LYP and 6-311G (d, p) level, like internal thermal energy (E), constant volume heat capacity (C<sub>v</sub>), and entropy (S), have been calculated and listed in Table 4. At the room temperature, conduction band is almost empty so electronic contribution in total energy is negligible. Thermodynamic parameters clearly indicate that vibration motion plays a crucial role in assessing thermo dynamical behavior of title compounds.



**Fig. 2** HOMO- LUMO and MESP pictures of 4-chloro-3-ethylphenol

**Table 2** Total Energy, HOMO, LUMO, Energy Gap and Dipole Moment of 4-chloro-3-ethylphenol.

S. No.	Parameter	Value
1	Total Energy E (a.u.)	-0.06600900
2	HOMO	-0.33787 au
3	LUMO	0.00101 au
4	Frontier Orbital Energy Gap	9.217536 eV
5	Dipole Moment (Debye)	1.0071

**Table 3** Mulliken Atomic Charges of 4-Chloro-3-ethylphenol.

S. No.	Atom	Atomic charge
1.	C	0.107435
2.	C	-0.191797
3.	C	-0.056775
4.	C	-0.166471
5.	C	-0.027535
6.	C	-0.148047
7.	H	0.113537
8.	H	0.114205
9.	H	0.134727
10.	O	-0.225227
11.	H	0.197640
12.	Cl	0.063861
13.	C	-0.063103
14.	C	-0.112843
15.	H	0.043406
16.	H	0.042035
17.	H	0.045693
18.	H	0.066408
19.	H	0.062852

5

**Table 4** Thermodynamic Properties of 4-chloro-3-ethylphenol

Parameter	E (Kcal/mol)	C <sub>v</sub> (Cal/mol-K)	S (Cal/mol-K)
Total	101.161	36.127	96.882
Translational	0.889	2.981	41.044
Rotational	0.889	2.981	30.340
Vibrational	99.384	30.166	25.497

### Assignment of fundamentals

10 4-Chloro-3-ethylphenol has 19 atoms 51 normal modes of vibration. We made a reliable one-to-one correspondence between the fundamentals and the frequencies calculated by B3LYP/6-311 G (d, p) method. The relative band intensities are also very satisfactory along with their positions. Some important  
15 modes are discussed hereafter. The harmonic- vibration frequencies are calculated for the title molecule, and are given in Table 5.

20

**Table 5** Calculated Wave Numbers and respective IR intensities of 4-chloro-3-ethylphenol

Frequency	IR intensity	Vibrational assignment
56	0.224	(C-CH <sub>2</sub> -CH <sub>3</sub> ) bend from joint of ring
97	0.9341	Twist in whole molecule from middle
147	0.809	Twist CH <sub>3</sub>
219	0.664	w (C-Cl)
223	0.6098	Twist CH <sub>3</sub>
271	27.4195	Twist (C-OH)
273	60.1929	γ (C-C-C)
313	9.4148	γ (C-C-C)
363	0.0335	τ (C-C-C-C)
401	5.1796	Twist C-CH <sub>3</sub>
430	6.8224	Twist C-CH <sub>3</sub>
505	2.7302	w (C-OH)
543	0.9521	τ (C-C-C-C)
577	1.8506	γ (C-C-C)
630	13.3434	Ring breathing
682	0.8848	γ (C-C-C)
767	3.2385	τ (C-C-C-C)
815	9.933	Twist CH <sub>2</sub>
825	29.7075	Twist CH <sub>2</sub> + γ (C-C-H)
918	31.2325	γ (C-C-C) + γ (C-C-H)
951	5.6351	γ (C-C-C) + γ (C-C-H)
977	1.5212	Twist CH <sub>2</sub>
1014	2.9778	Twist CH <sub>2</sub>
1067	4.5797	β (C-C-C) + β (C-C-H)
1073	11.8792	β (C-C-C)
1091	1.0733	Rock CH <sub>2</sub>
1124	13.6078	β (C-C-H) + Twist CH <sub>2</sub>
1132	0.4615	Twist CH <sub>2</sub> + Twist CH <sub>3</sub>
1171	15.2255	β (C-C-H)
1213	12.8524	β (C-C-H)
1242	43.6206	β (C-C-C)
1297	2.617	β (C-C-H)
1341	4.7889	S (H-C-H)
1355	52.7334	β (C-O-H)
1374	0.0902	S (H-C-H)
1378	1.5549	S (H-C-H)
1402	0.3855	S (H-C-H)
1434	15.9766	Ring breathing
1561	97.5924	v(C-O)
1577	80.9833	v(C-C)
1733	30.9453	v(C-C)
1756	27.2358	v(C-C)
2867	1.9307	v(C-H)
2935	43.2103	v(C-H)
2945	3.7088	v(C-H)
2976	2.4958	v(C-H)
2980	11.0092	v(C-H)
2995	41.5051	v(C-H)
3015	0.1693	v(C-H)
3096	0.1664	v(C-H)
3794	22.6805	v(O-H)

25

### Normal mode analysis

The O-H stretching vibrations are normally viewed in the region 3400-3700 cm<sup>-1</sup>. A strong O-H stretching vibration, presented at

3794  $\text{cm}^{-1}$  in calculated spectrum. We have seen in literature that the C–H stretching vibrations are usually observed in 2800– 3200  $\text{cm}^{-1}$  region. In this study, the (C–H) functional group, presented at 2935 and 2995  $\text{cm}^{-1}$  in calculated spectra in calculated data. A strong C-C stretching vibration, presented at 1577 and 1733  $\text{cm}^{-1}$  in calculated spectrum while 1561  $\text{cm}^{-1}$  for C-O stretching vibration. A strong scissoring vibration {S (H-C-H)} is presented at 1341  $\text{cm}^{-1}$  in theoretical vibrational spectra. Some in and out of plane bending and rocking vibrations due to C-H are also presented in the assignment of title molecule.

As expected, torsion modes along with wagging modes appear in the lower frequency range. A strong torsion mode of C-C-C-C is at 767  $\text{cm}^{-1}$  in calculated spectrum while strong wagging mode is at 505  $\text{cm}^{-1}$  in calculated spectrum. There are some frequencies in lower region having appreciable IR intensity. Furthermore, the study of low frequency vibrations are of great significance, because it gives information on weak intermolecular interactions, which take place in enzyme reactions [16]. Knowledge of low frequency mode is also essential for the interpretation of the effect of electromagnetic radiation on biological systems [17]. The aim of vibrational analysis is to acquire direct information on lower and higher frequency vibrations of title molecule. No experimental FTIR spectrum is available for comparison of title molecule so it will provide a suitable path for experimental researchers.

## Conclusion

We have done a Structural, electronic, and vibrational properties of 4-Chloro-3-ethylphenol Using DFT theory. All frequencies are real in the molecule. Hence the compound is stable. Reactivity reflects the susceptibility of a substance towards a specific chemical reaction and plays a key role in, for example, the design of new molecules and understanding biological systems and material science. The present work might encourage the need for an extensive study by the experimentalists interested in the vibrational spectra and the structure of this compound.

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## Notes and References

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