

## Study the Pollutants Chlorophenols: Electronic and Physical Properties Relationship

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### Abstract

Geometrical optimization and electronic structure of chlorophenols were researched by DFT (B3LYP) utilizing a 3-21G basis set. We have likewise researched the aggregate electronic properties, Highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and energy gap. The calculated HOMO and LUMO energies demonstrate that charge transfer occurs within the molecule.

**Keywords:** Chlorophenols; Electronic; Physical properties; Molecular orbital

دراسة الملوثات الكلوروفينولية: علاقة الخواص الإلكترونية والفيزيائية

### الخلاصة

تم بحث ودراسة الشكل الهندسي الأمثل، والتركييب الإلكتروني للمركبات الكلوروفينولية بواسطة نظرية دالة الكثافة (B3LYP) DFT باستخدام G21-3 كمجموعة الأساس. لقد بحثت كذلك

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الخصائص الكلية الإلكترونية والاوربتال الجزيئي المشغول الأعلى HOMO والاوربتال الجزيئي الفارغ الأدنى LUMO وفجوة الطاقة.

**الكلمات المرشدة:** الكلوروفينولات، خواص فيزيائية، الاوربتال الجزيئي، الكتروني.

## INTRODUCTION

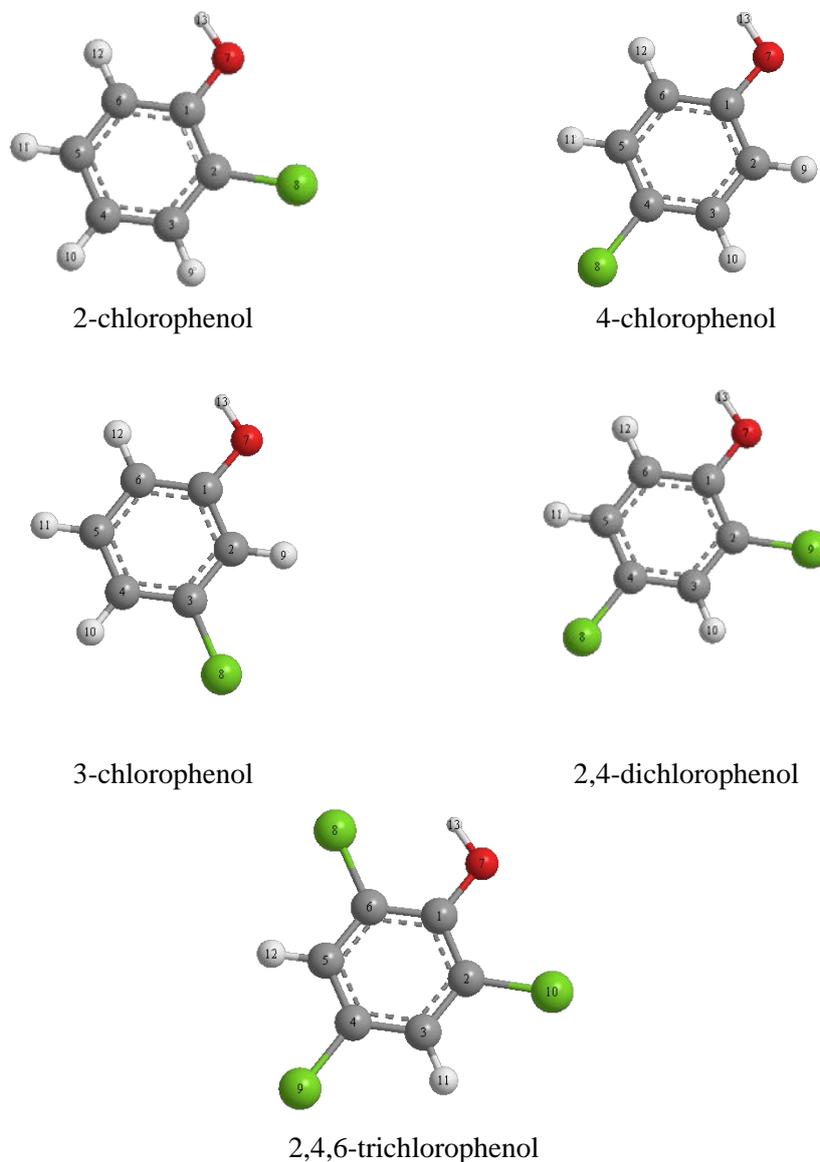
Hypothetical studies for phenols are interesting because of their generally size and comparability to natural species [1,2]. Chlorophenols are compounds in which chlorine and hydroxyl have been added to benzene. Dissociation degree of halogenated phenols was expansion with increment of chlorine atoms [3]. Chlorophenols have been utilized as germ-killers, pesticides and certain contaminants are available in the crude water [4]. Theoretical studies are fundamental tool for interpretations, forecast of vibrational spectrum, molecular geometries and foreseeing different properties [5,6]. Density functional concept offers different utilization of reasonable computational techniques, which could deal with generally great molecules [7]. There are 19 different chlorophenols, five of them had been examined in this paper, named: 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol. All of topics are solid at room temperature yet 2-chlorophenol is a liquid. All the compounds talked about, are produced commercially. In the present work, we have concentrated on the structure of chlorophenols, by utilizing Density Functional Theory (DFT) method. The DFT estimations had been performed to support wave number assignment, thermodynamic properties and HOMO-LUMO properties. This study may give valuable data about the molecular geometry, HOMO-LUMO and thermodynamic property of chlorophenols.

## The Calculation Method

To compute the ground-state geometry, Gaussian 03, Revisions C.01 and polarization premise sets (3-21G) [8,9]. A combination of the Becke three-parameters hybrid (B3) [10] exchange utilitarian and the Lee-Yang-Parr (LYP) [11] relationship useful (B3LYP) [12,13], an interpretation of the DFT [14,15] was utilized to focus all enhanced geometries, EHOMO, ELUMO and physical properties for the chlorophenols in this study.

## Results and Discussion

Density Function Theory estimations were utilized for the chlorophenols 1-5, and the optimized structures of the highest stable structures are verified in Figure 1.



**Figure (1). The most stable geometrical structures for chlorophenols 1- 5**

Energies and molecular orbital that give a complete explanation of the orbital with the spatial features, nodal patterns and individual atom commitments are available in Table 1.

**Table (1). Total energy in Kcal/mol, Potential energy in Kcal/mol, Kinetic energy in Kcal/mol and dipole moment in Debye for chlorophenols 1-5**

Compound	Total Energy	Potential Energy	Kinetic Energy	Dipole
1	-477265.2519	-953908.991	476643.7391	4.099897
2	-478739.7965	-955164.6825	476424.886	3.834976
3	-478739.421	-955165.9651	476426.5442	3.001606
4	-765717.4132	-1528332.0836	762614.6704	3.715716
5	-1052696.2852	-2101495.6254	1048799.3403	1.540521

The critical theoretical parameters for the considered chlorophenols are HOMO-LUMO, the most reactive position and types of reaction in  $\pi$ -electron systems [16]. It can be characterized the conjugated molecules by a little HOMO and LUMO division, which is the intermolecular charge exchange through  $\pi$  conjugated system for donating gatherings to the electron withdrawals one [17]. HOMO and LUMO are the primary orbital that joins in the stability of the molecules, they represent capacity for giving and tolerating an electron additionally, they are for the most part  $\pi$ -anti-bonding type orbitals and the difference between EHOMO and ELUMO orbital is named energy gap (Table 2). On the off chance that the gap between Highest Occupied Molecular Orbital and the Lowest Unoccupied Molecular Orbital are large in the electronic system that mean, the molecules ought to be less reactive as compared with the small gap. Stability, reactivity, polarizes-ability and chemical hardness-softness can be dictated by an energy gap of the molecule. These days the scientists in organic field likewise consider the HOMO and LUMO for the molecules because it clarifies the eventual charge transfer interaction within the Molecule and that affects the biological activity for the studied molecules. The three dimension plots of HOMO and LUMO for the contemplated chlorophenols are shown in Figure 2. The red color speaks to the positive phase while the blue one represents the negative phase. From Figure 2, it can be shown that the Highest Occupied Molecular Orbital were found on the chloride and benzene ring while the Lowest Unoccupied Molecular Orbital one located in the conjugated system of the benzene ring and thusly the substitution chlorides have contributed of electron gift capacity through inductive impact while benzene ring has a capacity of electron acceptance by means of resonance impact. The orbital energy levels of Highest Occupied Molecular Orbital and the Lowest Unoccupied Molecular Orbital of contemplated chlorophenols 1-5 are recorded in Table 2.

**Table (2). HOMO and LUMO energies (eV) of compounds 1-5**

Compound	HOMO	LUMO	Energy gap
1	-11.275	-0.015	-11.26
2	-12.184	-0.563	-11.621
3	-11.215	-1.076	-10.139
4	-10.674	-0.303	-10.371
5	-10.248	-0.682	-9.566

For the examined chlorophenols, the gap values between HOMO and LUMO for the first compound named 2-chlorophenol is -11.26 eV while for the second compound that named 3-chlorophenol is -11.621eV, additionally for the rest examined chlorophenols named "4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol " were -10.139 eV, -10.371eV and -9.566 eV respectively. The energy gap values between the HOMO and LUMO were little and that mean the inevitable charge transfer interaction occurring inside the chlorophenols furthermore the estimations of Highest Occupied Molecular Orbital for concentrated chlorophenols demonstrate that they had low ionization energies and they could lose electrons [18,19]. The HOMO for compounds 1-5 is placed over the benzene ring, hydroxyl and chloro, the HOMO-LUMO transition intimates an electron density transfer to benzene ring from O-H and C-Cl bonds. The little estimation of band gap reflects the chemical activity of the molecule. If there should be an occurrence of LUMO, the electron densities were localized on benzene ring and oxygen atom only in compounds 1 and 5. Whereas in only compounds that the chlorine in position 2 and 5 as in compounds 1, 4 and 5 the electron densities were full localized in benzene ring and chlorine atom position too. HOMO to LUMO transition indirectly way clarifies the descriptor of electron advocate and acceptor keeping in mind the end goal to comprehend their associating capacity with their target molecules.

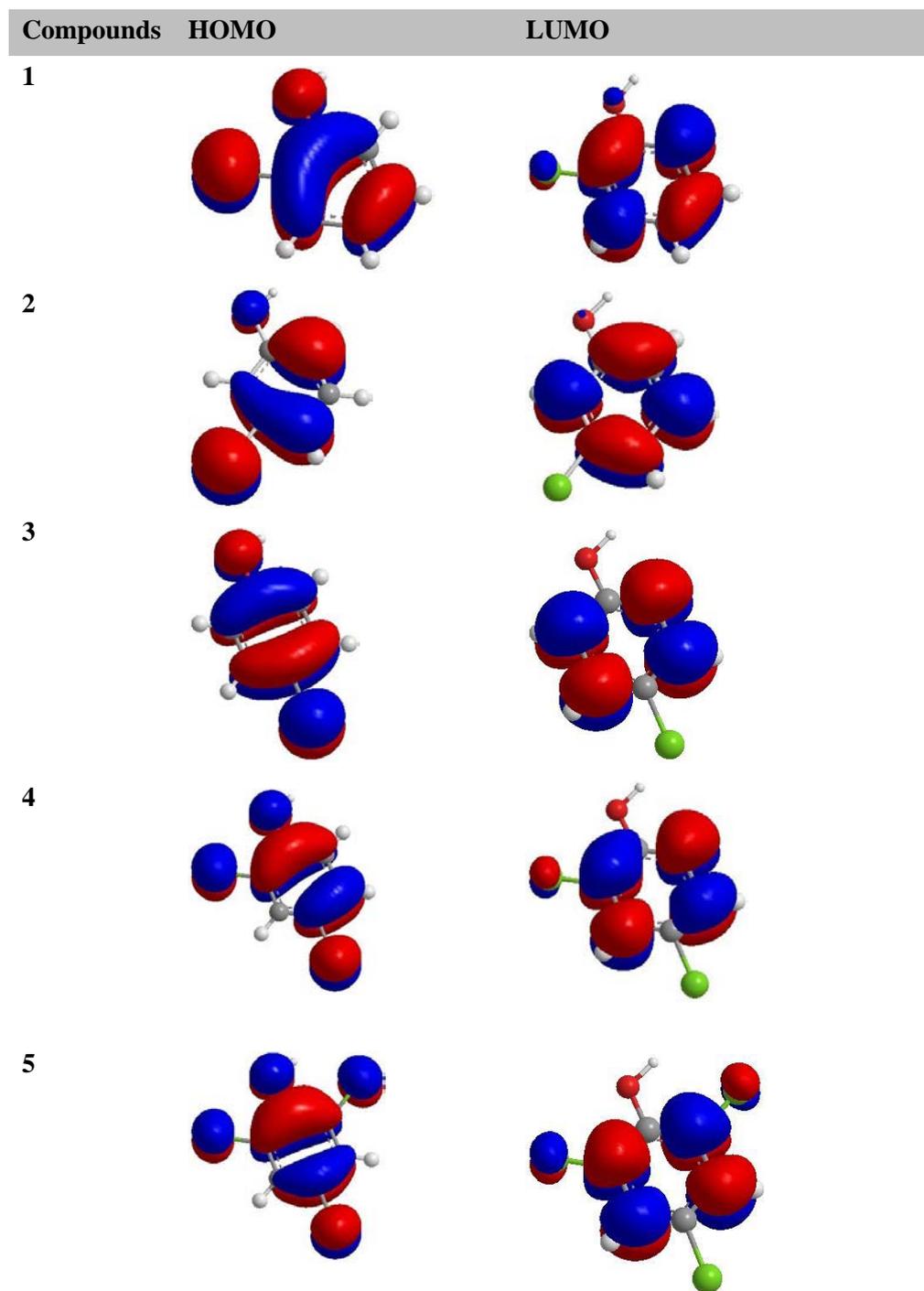


Figure (2). Highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital of compound 1-5

### Mulliken and Lowdin Charges

The estimations of Mulliken and Lowdin charges have important roles in the theoretical chemistry application due to atomic-charges impact dipole-moment, molecular polarizability, electronic-structures, and a lot of properties of molecular-systems Tables 3 and 4. A prior study [20] had verified that the atomic-charges were influenced by existence of substituent of the rings. Furthermore, with the assistance of a reference model, compounds 1-5 with improved geometries and 3D geometrical structures are given in Figure 1. Information presented in Tables 3 and 4, indicated that the most noteworthy Mulliken atomic charge in compound 1 is at [O(7) -0. 72727] emulated by the following charge value at [C(5) -0. 36241] likewise the most noteworthy Lowdin atomic charge in the compound 1 is at [O(7) -0. 317859]. This information obviously demonstrated that the atoms were most reactive in the direction of adding substitution reactions. Information for compound 2 is at [O(7) -0. 594429] took after by the following charge esteem at [C(4) -0. 260] additionally the highest Lowdin atomic charge in compound 1 is at [O(7) -0. 246465] took after by the following charge esteem at [C(1) -0. 168876]. For the compounds 3-5 the highest Mulliken and Lowdin atomic charges were at [O(7)] and took after by the following charge value at [C(5) and C(1)].

**Table (3). Mulliken charges of compound 1-5**

2-CP	Charge	3-CP	Charge	4-CP	Charge	2,4-DCP	Charge	2,4,6-TCP	Charge
C(1)	-0.276	C(1)	-0.217	C(1)	-0.203	C(1)	-0.195	C(1)	-0.2763
C(2)	-0.223	C(2)	-0.177	C(2)	-0.156	C(2)	-0.156	C(2)	-0.129
C(3)	-0.252	C(3)	-0.163	C(3)	-0.264	C(3)	-0.269	C(3)	-0.269
C(4)	-0.178	C(4)	-0.264	C(4)	-0.159	C(4)	-0.124	C(4)	-0.124
C(5)	-0.362	C(5)	-0.154	C(5)	-0.174	C(5)	-0.288	C(5)	-0.286
C(6)	0.453	C(6)	0.297	C(6)	0.287	C(6)	0.338	C(6)	0.387
O(7)	-0.727	O(7)	-0.594	O(7)	-0.595	O(7)	-0.577	O(7)	-0.573
Cl(8)	0.135	Cl(8)	0.084	Cl(8)	0.078	Cl(8)	0.099	Cl(8)	0.123
H(9)	0.248	H(9)	0.183	H(9)	0.187	Cl(9)	0.137	Cl(9)	0.157
H(10)	0.255	H(10)	0.201	H(10)	0.218	H(10)	0.198	Cl(10)	0.106
H(11)	0.252	H(11)	0.214	H(11)	0.219	H(11)	0.225	H(11)	0.251
H(12)	0.278	H(12)	0.231	H(12)	0.214	H(12)	0.245	H(12)	0.251
H(13)	0.402	H(13)	0.359	H(13)	0.357	H(13)	0.366	H(13)	0.382

Table (4). Lowdin charges of compound 1-5

2-CP	Charge	3-CP	Charge	4-CP	Charge	2,4-DCP	Charge	2,4,6-TCP	Charge
C(1)	-0.172	C(1)	-0.168	C(1)	-0.158	C(1)	-0.148	C(1)	C(1)-0.11
C(2)	-0.070	C(2)	-0.072	C(2)	-0.087	C(2)	-0.087	C(2)	-0.093
C(3)	-0.122	C(3)	-0.123	C(3)	-0.079	C(3)	-0.073	C(3)	-0.070
C(4)	-0.072	C(4)	-0.045	C(4)	-0.086	C(4)	-0.091	C(4)	-0.091
C(5)	-0.120	C(5)	-0.136	C(5)	-0.121	C(5)	-0.097	C(5)	-0.093
C(6)	0.163	C(6)	0.116	C(6)	0.107	C(6)	0.102	C(6)	0.099
O(7)	-0.317	O(7)	-0.246	O(7)	-0.248	O(7)	-0.229	O(7)	-0.222
Cl(8)	-0.006	Cl(8)	-0.021	Cl(8)	-0.027	Cl(8)	-0.011	Cl(8)	0.007
H(9)	0.104	H(9)	0.096	H(9)	0.098	Cl(9)	0.015	Cl(9)	0.032
H(10)	0.109	H(10)	0.105	H(10)	0.116	H(10)	0.104	Cl(10)	0.002
H(11)	0.109	H(11)	0.114	H(11)	0.117	H(11)	0.120	H(11)	0.136
H(12)	0.123	H(12)	0.126	H(12)	0.114	H(12)	0.133	H(12)	0.136
H(13)	0.273	H(10)	0.255	H(13)	0.254	H(13)	0.262	H(13)	0.270

### Conclusions

In this research paper, compounds marked 1-5 have been considered hypothetically utilizing DFT (Density Functional Theory), their atomic-charges and stereochemistry were assessed, and it was observed that they are nonplanar. MO (Molecular orbital) estimations in like manner are consider and have given point of interest depiction of the orbitals, spatial features, nodal shapes, and the contributions of specific atoms.

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