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# Theoretical Study Chlorohydroquinone Molecule With Substituted Lithium Via Quantum Computation Approach

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**ABSTRACT**

This is the first theoretical report on chlorohydroquinone (2-chlorobenzene-1,4-diol) molecules formed by adding lithium to the ortho position of the benzene ring. Our extensive examination of the Chlorohydroquinone (2-chlorobenzene-1,4-diol compounds) molecule utilizing DFT/6-31G++(d) basis set Gaussian program simulations and substituted lithium (Li) revealed crucial chemical characteristics. The fundamental purpose of this research was the theoretical computational investigation of the chlorohydroquinone molecule by Li. Theoretical computations were conducted to understand the physical and electronic properties of this compound, including its $E_{HOMO}$, $E_{LUMO}$, band gap (EG), ionization energy (IA), electron affinity (EA), absolute electronegativity (χ), global hardness (η), and global softness (S), U-V spectroscopy, and electrostatic potential (ESP) map. The 2-chlorobenzene-1,4-diol - Lithium compound, with a reduced energy gap of 2.619 eV, exhibits strong electronic distribution, low chemical stability, high electrical conductivity, and high reactivity.

## 1. Introduction

Chlorophenols (CPs) are a common type of persistent organic pollutant that may be extremely harmful to human health. They are found in wastewater and accumulate in organisms through the food chain [1, 2]. 2-chlorohydroquinone (H2QCl), one of the CPs, has been employed as a developing agent, fungicide, and pharmaceutical intermediary. A benzene ring, a -OH group, and one or more atoms of chlorine connected to the ring are the characteristics of chlorophenols. The electrophilic group radical targets the electron-rich regions at the ortho- and para-sites because the phenyl (Ph) rings, OH groups, and Cl groups in the ortho- and para-position concern one another [3-5]. Because H2QCl is very dangerous and has a low concentration in water, a quick and sensitive analytical approach must be established to identify and detect it. Thus far, high-performance liquid chromatography (HPLC) and other traditional techniques for the identification of organic pollutants have been the primary means of determining H2QCl.

Chlorohydroquinone is a significant result of the photocatalytic degradation of chlorophenol. In the nitrogen-or air-free solution, chlorohydroquinone (H2QCl) is photolyzed to hydroquinone (QH2) and chlorobenzoquinone (QCl) during the process. Then, an inverse reaction takes place, producing QH2 and photolyzing it to create H2QCl. Furthermore, acetic, maleic, and fumaric acids are produced by further oxidation of this QCl and other hydroxylated products by decarboxylation, which splits the aromatic rings [6, 7].

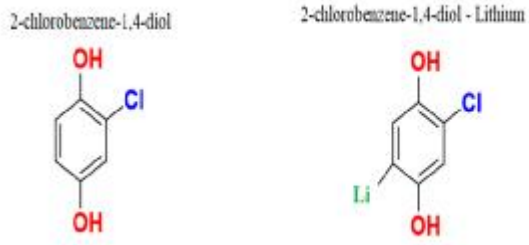


**Fig. 1.** 2-chlorohydroquinone-1,4-diol structure

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A substance in chemistry known as H2QCl has been used as an aromatic agent. It's an ether, alcohol, and water-soluble white crystalline solid. Also called 2-chlorohydroquinone-1,4-diol as seen in Figure 1. With a molecular weight of 144.55 g/mol and a chemical formula of C6H5ClO2, the mass-charge ratio (m/z) is 143. Ph molecule H2QCl is used as an intermediate in several various chemical industries, but it poses a serious risk to the environment. They are utilized in research labs, plastics, and insecticides. Additionally, it can be used as a fungicide, developmental agent, and pharmacological intermediary, among other things. H2QCl's propensity to seep into natural water is increasing with its widespread usage, and even at low concentrations, it might have disastrous effects on the biological environment [2, 8-10].

These characteristics are crucial for comprehending the structure-function relationships of molecules, forecasting their behavior in diverse settings, creating new materials with particular properties, and developing fields like materials science, drug discovery, and the chemical synthesis of compounds containing chlorohydroquinones**(**2-chlorobenzene-1,4-diol) by substituting lithium (Li) element. Through the use of DFT to examine these characteristics in chlorohydroquinone molecules, the study advances our knowledge of molecular behavior and offers insights that apply to a variety of scientific fields.

## 2. Methodology

For this study, we employed the Gaussian 09 computer tool to do arithmetic at the Density Functional Theory (DFT)/B3LYP level of theory [11-14]. The 6-31G ++(d) basis set was used to optimize the structure of Chlorohydroquinone **(**2-chlorobenzene-1,4-diol). This study aims primarily to theoretically and computationally examine the 2-chlorobenzene-1,4-diol molecule by substituting lithium (Li) element. The study included analyzing shape-optimized structures to determine several electrical parameters, including energy gap (Eg), electronegativity (χ), softness (S), hardness (H), chemical potential (Pi), uv spectroscopy, and electrostatic potential (ESP) map.

## 3. Result And Discussion

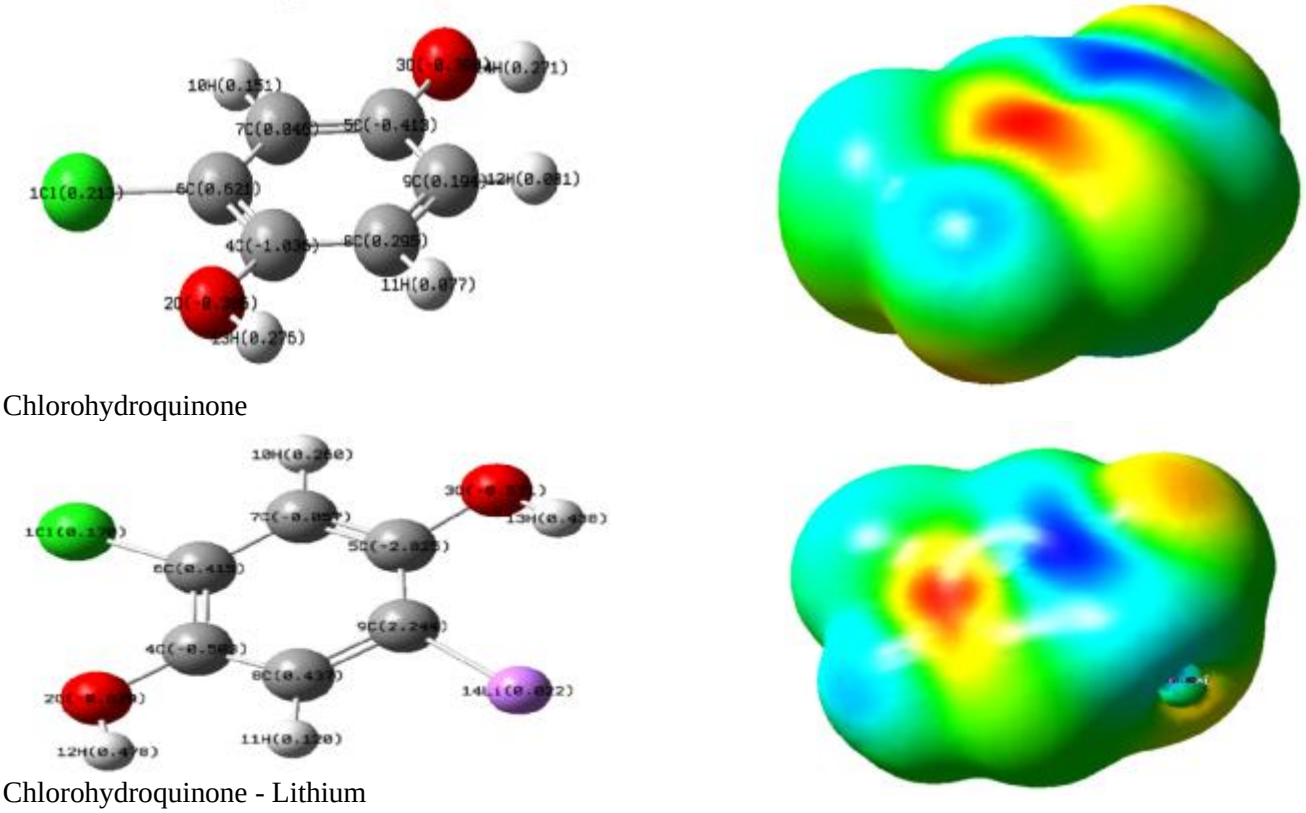
### Geometric Shape

According to the data shown in Figure 1, the optimal shape was produced by using the Gaussian software in combination with the DFT/ 6-31G ++(d) basis that was adjusted to correspond with the structure of the Chlorohydroquinone (2-chlorobenzene-1,4-diol). It is important to note that molecules have their unique orbitals, which are separate from the orbitals that are found in atoms. The first stage of a geometry optimization strategy that is beneficial for this approach focuses on the energy that is associated with a certain starting molecule shape. This technique may be used for this approach [14-16]. The physicochemical characteristics and chemical interactions of the compounds 2-chlorobenzene-1,4-diol, and 2-chlorobenzene-1,4-diol - Lithium are influenced by electrostatic potential (ESP) maps and electron charge densities, as seen on the right side of Figure 2. The addition of Lithium (Li) caused a modification in the charge distribution of 2-chlorobenzene-1,4-diol molecules, as reported. Quantitatively illustrates the generation of an electric potential around molecules at a certain location and point r (measured in atomic units).

Molecular electrostatic potential (MEP) analysis is a potent technique used to investigate the distribution of charge inside a molecule. MEP analysis establishes a connection between the physiochemical properties of the system, such as chemical reactivity, dipole moment, and partial charges, and the geometric form of the system [17]. The ESP is influenced by many elements, such as partial charges, electronegativity, dipolar moment, and the spatial arrangement of chemical processes inside the molecular structure. The color zones associated with each molecule are correlated with different electronegativities, which are listed in the following order: The electronegativity values for the elements are as follows: O=3.44> C=2.55> H = 2.20.> Li=0.98 eV. In an electrostatic potential map, regions exhibiting higher electronegativity are often associated with redder areas, indicating a greater negative potential. Conversely, regions with a low electronegativity would appear as more positively charged (bluer) regions. The element blue has a greater amount of positive charge, a reduced electron density, and a diminished proton affinity [18].

### Global Activities

The values of the molecular orbital parameters that were computed during the study to investigate the chemical reactivity are shown in Table 1. It was necessary to determine the energies that correspond to the HOMO-LUMO states to successfully calculate the global reaction parameters. The DFT/B3LYP level of theory (method) on the foundation sets 6-31G ++(d,) was used to ascertain the HOMO-LUMO [14, 17]. On display in Figure 3 are the energy gap, the connections between the HOMO and LUMO of compounds, and the front molecular orbital (FMO) diagrams.



Chlorohydroquinone

Chlorohydroquinone - Lithium

**Fig. 2.** Geometry optimization, and ESP map with the DFT method, 6-31G +(d) basis set

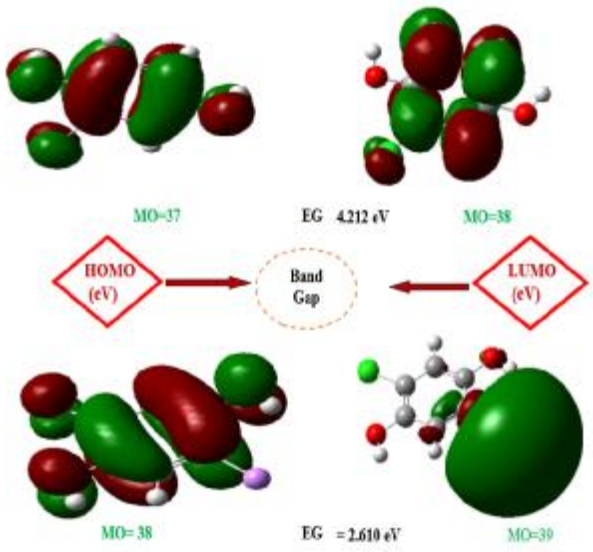



**Fig. 3.** Front molecular orbital (FMOs) for the title compounds DFT/ **6-31G ++(d)**

The expression "$E_{HOMO}$-$E_{LUMO}$ energy gap" is used in molecular orbital theory to denote the least energy required to transition a molecular orbital from its occupied state to its unoccupied state. In molecular orbital theory, the term "$E_{HOMO}$-$E_{LUMO}$ energy gap" refers to the minimum energy needed to transition a molecular orbital from its occupied state to its unoccupied state [15, 19].

According to **Table 1**, the 2-chlorobenzene-1,4-diol - Lithium molecule, which has an energy gap of 2.610 eV, exhibits traits such as abundant electronic dispersion, limited chemical stability, elevated electrical conductivity, and notable reactivity. The energy gap with the lowest value (2.610 eV) Chlorohydroquinone-Lithium exhibits a significant electronic spread between the donor and acceptor orbitals. According to **Table 1**, molecular hardnesses are listed from greatest to lowest: the 2-chlorobenzene-1,4-diol > the 2-chlorobenzene-1,4-diol - Lithium while molecular softness 2-chlorobenzene-1,4-diol - Lithium > the 2-chlorobenzene-1,4-diol compounds. The 2-chlorobenzene-1,4-diol - Lithium molecule has a softness of 0.383 $eV^{-1}$, which indicates that it is very capable of transferring electrons. From this, we might infer that a greater energy band gap corresponds to a reduced molecule softness. Electronegativity, denoted by the symbol $\chi$, quantifies an atom's capacity to attract and acquire an electron. A high electronegativity value of 2.865 eV for the 2-chlorobenzene-1,4-diol compounds indicates a strong ability of the element to attract electrons with a larger force [20, 21].

**Table 1.** Quantum chemical parameters using DFT/ 6-31G ++(d)

| **Parameters** | | **Chlorohydroquinone** | **Chlorohydroquinone- Lithium** |
|---|---|---|---|
| **HOMO (eV)** | ---- | -4.97156 | -4.15818 |
| **LUMO (eV)** | ---- | -0.75918 | -1.54813 |
| **Ionization energy (eV)** | $I = -HOMO$ | 4.972 | 4.158 |
| **Electron Affinity (eV)** | A= $-LUMO$ | 0.759 | 1.548 |
| **Energy gap (eV)** | $HOMO - LUMO$ | 4.212 | 2.610 |
| **Hardness (eV)** | $\eta = \frac{IE - EA}{2}$ | 2.106 | 1.305 |
| **Softness ($eV^{-1}$)** | $S = \frac{1}{\eta}$ | 0.237 | 0.383 |
| **Electronegativity (eV)** | $\chi = \frac{IE + EA}{2}$ | 2.865 | 2.853 |
| **Chemical potential (eV)** | $\mu = -\chi$ | -2.865 | -2.853 |

**UV- Spectroscopy**

The discovery of molecular structure was probably achieved by chemists using UV-visible spectroscopy at first. Optical tools have made it possible to better study the optical and electrical properties of nanoscale particles [22]. The absorbance spectrum is shown in **Figure 4**. The Lithium-doped 2-chlorobenzene-1,4-diol structure's peak and absorbance spectra are shown in **Figure 4** for 6-31G ++(d,). The electronic shift from HOMO to LUMO is paralleled by the greatest absorption wavelength, according to the transition and absorption spectra [23]. Since lithium ions interact with the compound's molecular structure, the location of peaks changes when lithium is doped into the structure of 2-chlorobenzene-1,4-diol.

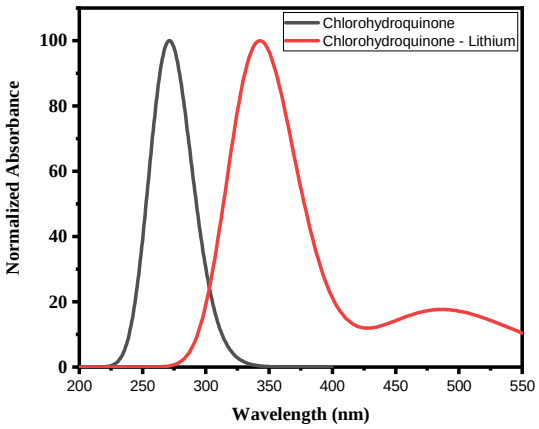



**Fig. 4.** UV-visible absorption spectrum

## 4. Conclusion

Finally, our thorough analysis using DFT/6-31G ++(d) basis set Gaussian program simulations and substituted halogens in the Chlorohydroquinone (2-chlorobenzene-1,4-diol compounds) compounds molecule provided important insights into their molecular characteristics. Information on electronic structure, chemical stability, and reactivity may be obtained from front molecular orbitals (FMOs), which include HOMO, LUMO, and other molecular orbitals. In an electrostatic potential map, regions exhibiting higher electronegativity are often associated with redder areas, indicating a greater negative potential. The energy gap with the lowest value (2.610 eV) exhibits a significant electronic spread between the donor and acceptor orbitals. The 2-chlorobenzene-1,4-diol - Lithium molecule has a softness of 0.383 $eV^{-1}$, which indicates that it is very capable of transferring electrons. A high electronegativity value of 2.865 eV for the 2-chlorobenzene-1,4-diol compounds indicates a strong ability of the element to attract electrons.

**Credit authorship contribution statement:**

Rayan Latif Nasih & Vardo Khalid Hussin: Writing – original draft, Data curation.
Rebaz Obaid Kareem: Methodology, and Investigation, Formal analysis, Data curation.
Othman Abdulrahman Hamad: Formal analysis.

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Data availability
Data will be made available on request.

## References

[1] A.O. Olaniran, E.O. Igbinosa, Chlorophenols and other related derivatives of environmental concern: properties, distribution and microbial degradation processes, Chemosphere, 83 (2011) 1297-1306.
[2] S. Ding, P. Tan, J. Wen, T. Li, W. Wang, Quantification of 2-chlorohydroquinone based on interaction between N-doped carbon quantum dots probe and

photolysis products in fluorescence system, Science of The Total Environment, 814 (2022) 152745.
[3] S. Schmid, P. Krajnik, R. Quint, S. Solar, Degradation of monochlorophenols by γ-irradiation, Radiation Physics and Chemistry, 50 (1997) 493-502.
[4] Z.J. Zhang Jiao, L.D. Liu DeQi, B.W. Bian WenJuan, C.X. Chen XiHua, Degradation of 2, 4-dichorophenol by pulsed high voltage discharge in water, (2012).
[5] C. Kwan, W. Chu, A study of the reaction mechanisms of the degradation of 2, 4-dichlorophenoxyacetic acid by oxalate-mediated photooxidation, Water research, 38 (2004) 4213-4221.
[6] A. Rossi, A. Tournebize, P. Boule, Phototransformation of chlorohydroquinone in aqueous solution, Journal of Photochemistry and Photobiology A: Chemistry, 85 (1995) 213-216.
[7] Y. Wang, Z. Shen, Y. Li, J. Niu, Electrochemical properties of the erbium–chitosan–fluorine–modified PbO2 electrode for the degradation of 2, 4-dichlorophenol in aqueous solution, Chemosphere, 79 (2010) 987-996.
[8] G. Asgari, A. Sidmohammadi, A.R. Rahmani, M.R. Samargandi, H. Faraji, Efficient decomposition of pentachlorophenol by a high photon flux UV/sodium hydrosulfite: Kinetics, intermediates and associated transformation pathway, Optik, 218 (2020) 164981.
[9] Y. Liu, Y. Zhao, J. Wang, Activation of peroxydisulfate by a novel Cu0-Cu2O@ CNTs composite for 2, 4-dichlorophenol degradation, Science of The Total Environment, 754 (2021) 141883.
[10] S. Chaliha, K.G. Bhattacharyya, Wet oxidative method for removal of 2, 4, 6-trichlorophenol in water using Fe (III), Co (II), Ni (II) supported MCM41 catalysts, Journal of hazardous materials, 150 (2008) 728-736.
[11] R.O. Kareem, H. Kebiroglu, O.A. Hamad, Investigation of Electronic and Spectroscopic Properties of Phosphosilicate Glass Molecule (BioGlass 45S5) and Ti-BioGlass 45S5 by Quantum Programming, Journal of Chemistry Letters, 4 (2024) 200-210.
[12] O.A. Hamada, R.O. Kareemb, Y.H. Azeezb, M.H. Kebiroğluc, R.A. Omerd, O.I.H. Zebarie, Quantum Computing Analysis of Naphthalene Compound: Electronic Structure, Optical, and Thermochemical Approaches using DFT and HF.
[13] Y.H. Azeez, R.O. Kareem, A.F. Qader, R.A. Omer, L.O. Ahmed, Spectroscopic Characteristics, Stability, Reactivity, and Corrosion Inhibition of AHPE-dop Compounds Incorporating (B, Fe, Ga, Ti): A DFT Investigation, (2024).
[14] R.O. Kareem, M.H. Kebiroğlu, O.A. Hamad, O. Kaygili, N. Bulut, Epinephrine Compound: Unveiling Its Optical and Thermochemical Properties via Quantum Computation Methods.
[15] O. HAMAD, R.O. KAREEM, O. Kaygili, Density Function Theory Study of the Physicochemical Characteristics of 2-nitrophenol, Journal of Physical Chemistry and Functional Materials, 6 (2023) 70-76.
[16] R.B. Nadr, B.S. Abdulrahman, Y.H. Azeez, R.A. Omer, R.O. Kareem, Quantum chemical calculation for synthesis some thiazolidin-4-one derivatives, Journal of Molecular Structure, 1308 (2024) 138055.
[17] M. Javed, M.U. Khan, R. Hussain, S. Ahmed, T. Ahamad, Deciphering the electrochemical sensing capability of novel Ga 12 As 12 nanocluster towards chemical warfare phosgene gas: insights from DFT, RSC advances, 13 (2023) 28885-28903.
[18] M. Karabacak, E. Yilan, Molecular structure, spectroscopic (FT-IR, FT-Raman, 13C and 1H NMR, UV), polarizability and first-order hyperpolarizability, HOMO and LUMO analysis of 4′-methylbiphenyl-2-carbonitrile, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 87 (2012) 273-285.
[19] A. Hariharan, P. Vadlamudi, SERS of Epinephrine: A computational and experimental study, Journal of Molecular Structure, 1246 (2021) 131163.
[20] T. Yadav, R. Sahu, V. Mukherjee, Molecular modeling and spectroscopic investigation of a neurotransmitter: Epinephrine, Journal of Molecular Structure, 1176 (2019) 94-109.
[21] O.A. Hamad, R.O. Kareem, P.K. Omer, Properties, Characterization, and Application of Phthalocyanine and Metal Phthalocyanine, Journal of Chemical Reviews, 6 (2024).
[22] J.D. Mottishaw, A.R. Erck, J.H. Kramer, H. Sun, M. Koppang, Electrostatic potential maps and natural bond orbital analysis: visualization and conceptualization of reactivity in Sanger's reagent, Journal of Chemical Education, 92 (2015) 1846-1852.