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Enhancing the characteristics of gasoline through the influence of terminal groups

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Abstract: The features of aromatic compounds, a crucial field of organic chemistry, are examined in this study. Since they belong to a class of organic compounds with a closed carbon ring system and electrons evenly distributed among the ring atoms, the goal of this study is to comprehend their physical and chemical characteristics, giving them chemical stability thanks to the resonance phenomenon. These substances follow Huckel's rule, which establishes how many electrons are needed to produce aromaticity It establishes the quantity of electrons needed to attain aromaticity. The simplest of these compounds is benzene (C_6H_6). The impact of terminal groups on the benzene ring will be studied in this study. The carboxyl (COOH), nitro (NO_2), methyl (CH_3), and hydroxyl (OH) groups were all investigated. According to the results, the groups (OH and CH_3) successfully increase the chemical activity by increasing the electron density, whereas the groups (COOH and NO_2) remove electrons from the ring and decrease activity. Instead of hydrogen atoms in the benzene ring, these groups were added in a (Ortho/Para/Meta) form using the DFT method with 6-31G basis functions for the B3LYP level. Using the Gaussian 05 program, the electronic characteristics of the assemblies were examined. lower energy gap than the original molecule was discovered in the recently investigated assemblies, indicating the possibility of materials with novel electronic characteristics.

Keywords: *Aromatic rings, Hackle's rule, Terminal groups, Energy gap, Aromaticity.*

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Introduction

The physical mechanism before determining aromaticity was discovered, the term "aromatic" was used because many of the compounds have a sweet scent[1]. According to Hackle's rule, an aromatic molecule is defined as a group of atoms that are covalently bound together [2]. The substitution reactions that occur on these are the most crucial techniques for their preparation[3]. It is possible to introduce electrophiles and uncleophiles into aromatics through substitution reactions. Reaction series are altered as a result of variation in substitution, which is connected to variations in equilibrium[4]. Depending on the type of substituent, groups of atoms can either increase the aromatic ring's reactivity or decrease it. Activating is the term for it, and deactivating is the term for less. When discussing reactions that are classified as electrophilic aromatic substitution, these two terms are used. The purpose of this work is to optimize the geometry and examine the electronic properties using B3LYP/6-31G ,the most crucial instruments for determining an insulator's, semiconductor's, or metal's ground state properties[5,6].

Parts Calculated

The accuracy of results is largely determined by the type of calculation used and the basis set selected. Slater type orbitals and Gaussian type orbitals are the two primary categories of basis sets [7]. In koopmans' theorem the IE(ionization energy) = -HOMO and the EA(electron affinity) = - LUMO. For every molecule, the forbidden energy gap is determined using the formula $E_{gap}=E_{LUMO}-E_{HOMO}$

The energy difference between two frontier orbitals is half of the hardness (H). There is a tiny energy gap in the soft molecule[8,9]. Soft molecules (S) will be more reactive than hard molecules as the following formula

$$S = 1/2H \quad ,,,.$$

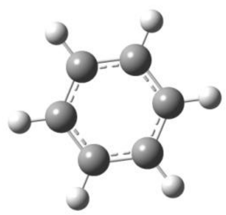
Since compensated groups have a significant impact on the distribution of electrons within the ring and, consequently, on benzene reactions, their effect on the ring has been studied [10-13]. The effects fall into two primary categories: those that target homogeneous centers (Ortho/Para), While the other groups are focused on heterogeneous centers (Meta), the carboxyl group (COOH) and the nitro group (NO_2) were examined. Additionally, the groups (hydroxyl OH, methyl CH_3) were examined[14].

Results and Discussion

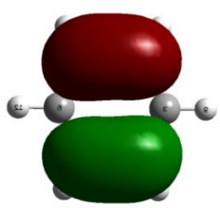
The Gaussian 09 package produces the results, and Gaussian View 5.0 builds the structure. compounds that are aromatic and are distinguished by the presence of double bonds, which creates a unique ring system, to create new structures with novel electronic characteristics by incorporating terminal groups to enhance the benzene ring's features. Either electron donors or electron withdrawers are these groups. Due to the oxygen atom's sole pair of electrons, which can split apart in the aromatic ring through resonance, the hydroxyl group contributes an electron [15]. This makes the electrons on the benzene ring denser, particularly in the ortho and para positions. The ring consequently becomes more reactive. Furthermore, the hydroxy group forms hydrogen bonds that affect the compound's physical properties and solubility. For benzene molecules and terminal hydroxyl groups (OH), the B3LYP was used to calculate the high occupied molecular orbital (HOMO) and the lower unoccupied molecular orbital (LUMO). The addition to the ring causes changes in the electronic states . Owing to the linear combination of atomic orbitals and molecular orbitals (LCAO-MO), the molecular orbitals are formed by the overlap of the atomic orbitals. For the molecules under study, the electronic states calculations are displayed in table (1). Benzene combines with other carbons to form single-carbon bonds. The small energy gap between the electronic states in table (1) compared to the benzene molecule indicates the ability to translate electrons across the energy band. Additionally, it is mentioned that these aggregates increase the benzene ring's electron density, which makes the ortho and para sites more reactive to electrophilic substances .As shown in figures (1 and 2), the other group, the methyl group (CH_3), contributes an electron density, albeit not as much as OH. The addition of a carboxyl group to benzene in figure (3) demonstrates that, under the right pressure and temperature conditions, the aromatic ring can participate in electrophilic substitution reactions. This process works well for creating derivatives of carboxylic benzene, which have a variety of uses in industry and medicine [16,17]. Considered a very negative electrolyte group, the nitro group (NO_2) draws electrons away from the benzene ring, increasing the reactivity of intermediate sites, as shown in figure (4).

Table (1): Computed energies for studied molecules.

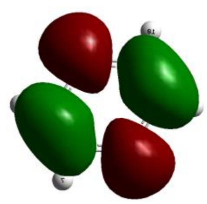
Species	Eg (eV)	E_T (eV)	-V/T	IE (eV)	EA (eV)	H (eV)	S $(eV)^{-1}$
C_6H_6	**6.6642**	**-6318.427**	**2.0060**	**6.788**	**-0.1238**	**3.3321**	**0.15005**
$C_6H_4(OH)_2$ (Meta)	**5.8817**	**-10410.486**	**2.0058**	**5.9538**	**-3.01295**	**2.94085**	**0.1700188**
$C_6H_4(OH)_2$ (Ortho)	**6.03467**	**-10410.186**	**2.0056**	**6.0978**	**0.06313**	**3.017335**	**0.1657091**
$C_6H_4(OH)_2$ (Para)	**5.4809**	**-10410.404**	**2.0056**	**5.771**	**0.2901**	**2.74045**	**0.1824517**
$C_6H_4(CH_3)_2$ (Meta)	**6.0312**	**-8457.706**	**2.0052**	**6.2739**	**-0.2427**	**3.0156**	**0.1658**
$C_6H_4(CH_3)_2$ (Para)	**6.0059**	**-8457.7137**	**2.0058**	**6.1699**	**-0.164**	**3.00295**	**0.1665**
$C_6H_4(CH_3)_2$ (Ortho)	**6.0153**	**-8457.7169**	**2.0052**	**6.2624**	**-0.2471**	**3.0076**	**0.1662**
$C_6H_4(COOH)_2$ (Meta)	**5.5721**	**-16577.4676**	**2.0056**	**7.6064**	**2.0343**	**2.78605**	**0.179465**
$C_6H_4(COOH)_2$ (Para)	**5.42264**	**-16577.02665**	**2.0056**	**7.3726**	**1.94996**	**2.71132**	**0.184412**
$C_6H_4(COOH)_2$ (Ortho)	**5.33262**	**-16577.45115**	**2.0056**	**7.572388**	**2.23977**	**2.66631**	**0.1875251**
$C_6H_4(NO_2)_2$ (Meta)	**4.168**	**-17443.34249**	**2.0068**	**8.4478**	**4.2798**	**2.084**	**0.239923**
$C_6H_4(NO_2)_2$ (Para)	**1.2428**	**-17443.342**	**2.0056**	**5.4962**	**4.2534**	**0.6214**	**0.8046347**
$C_6H_4(NO_2)_2$ (Ortho)	**3.77177**	**-17442.32315**	**2.0068**	**8.4856**	**4.71383**	**1.885885**	**0.2651275**



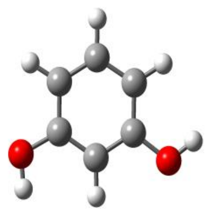
Benzen



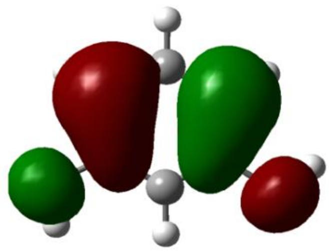
HOMO



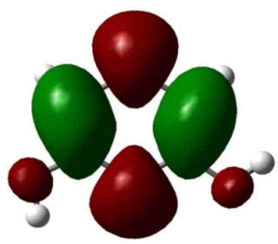
LUMO



Meta



HOMO



LUMO

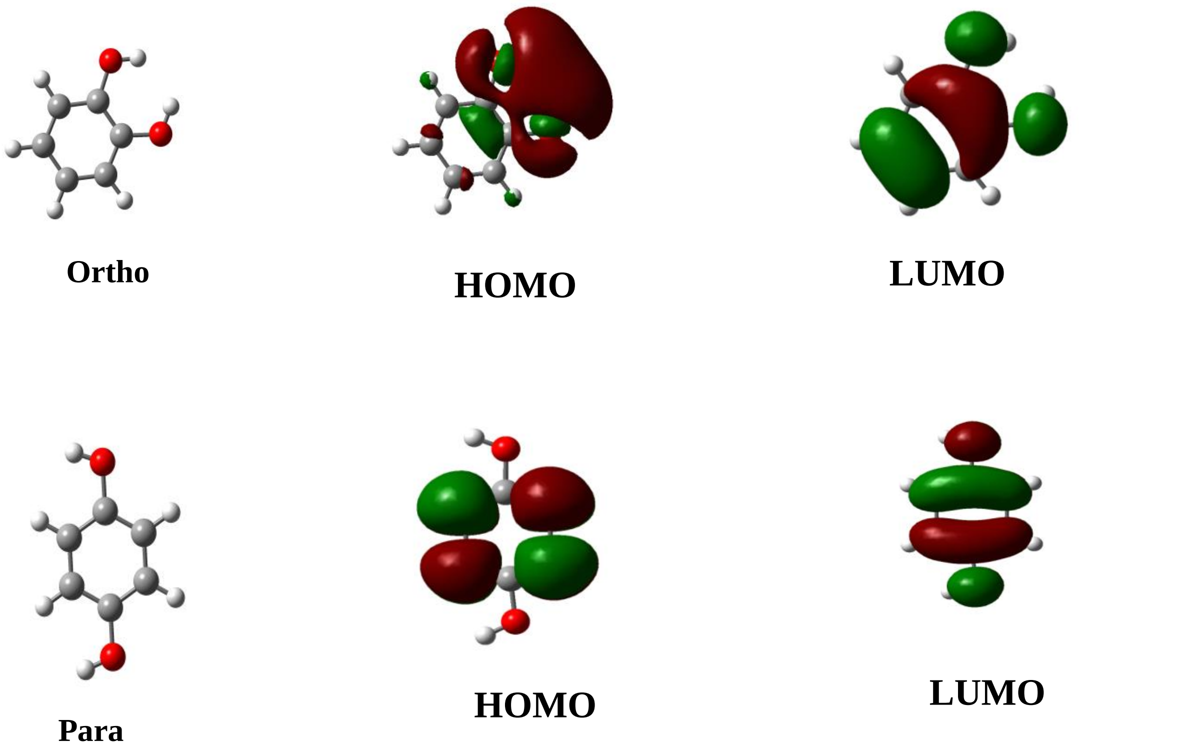
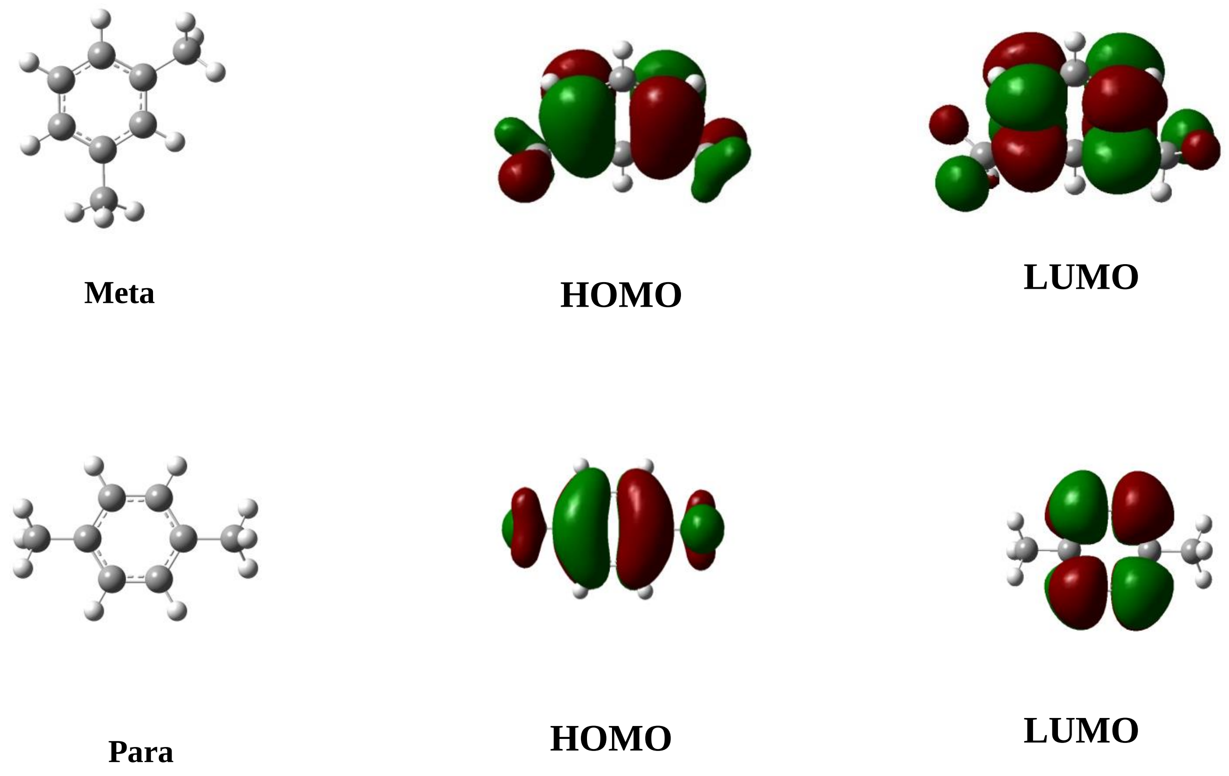
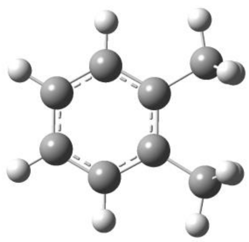
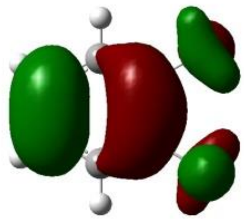


Figure (1): The optimal structures for terminal hydroxyl groups with HOMO and LUMO levels are displayed.

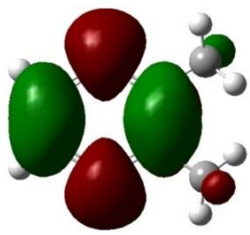




Ortho

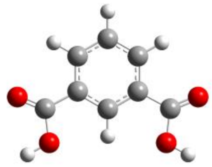


HOMO

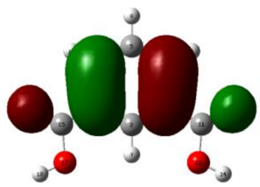


LUMO

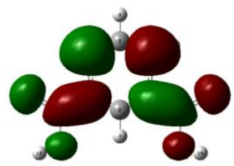
Figure (2): The HOMO and LUMO level-optimized structures for terminal methyl groups



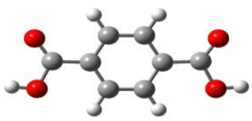
Meta



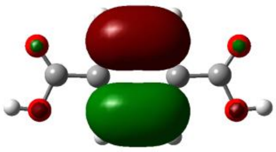
HOMO



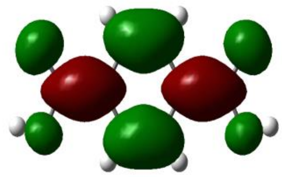
LUMO



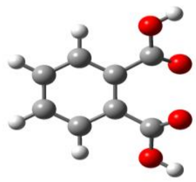
Para



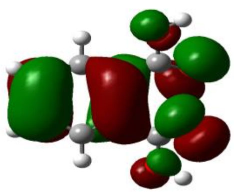
HOMO



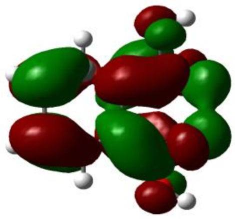
LUMO



Ortho

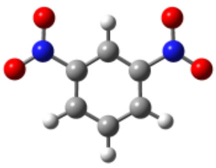


HOMO

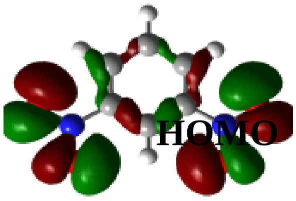


LUMO

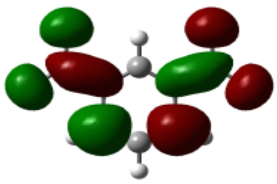
Figure (3): Displays the ideal arrangements for terminal carboxyl groups



Meta



HOMO



LUMO

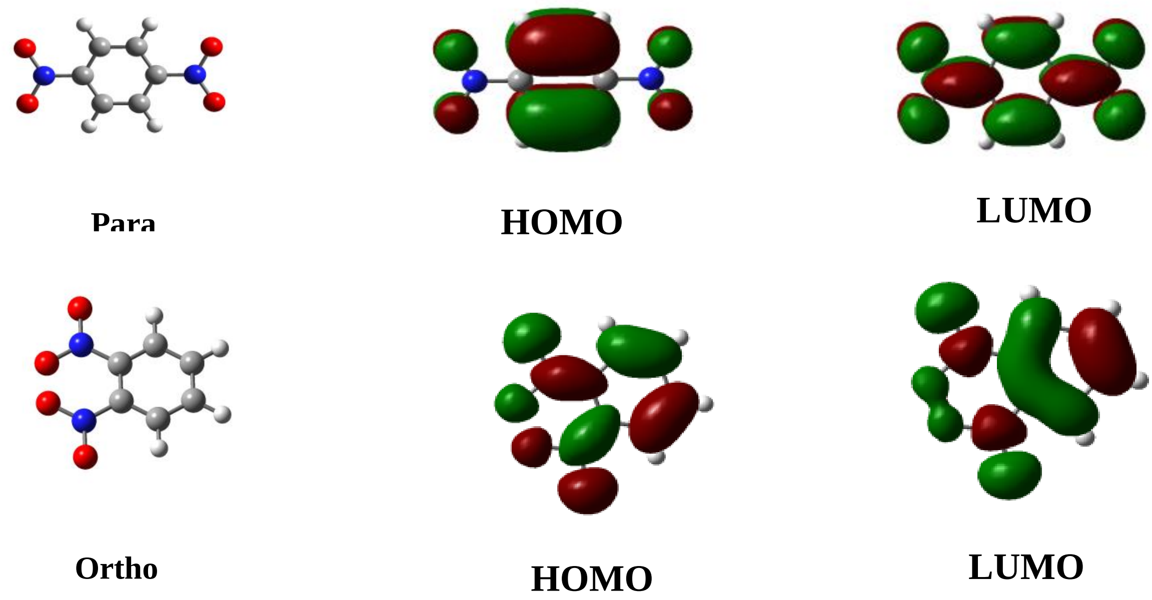


Figure (4): The ideal configurations for terminal nitro groups with HOMO and LUMO levels

Conclusion

When the electron-donating hydroxylase group OH is activated and directed towards ortho/para, the energy gap is reduced, resulting in a decrease in hardness and an increase in softness. This study's current method for optimizing the geometry of benzene has been found to be in good agreement with experiment data. A weak donor that is oriented toward ortho/para, the methyl CH_3 group marginally closes the energy gap. Thus the hardness decreases, the softness rises. Overall energy tends to drop a little .Hardness increases and softness decreases due to the electron-pullerant nature of the COOH carboxylic group. In order to increase the energy gap visibly, the nitro group NO_2 acts as a very powerful puller .While the softness is low, the hardness is high. While total energy is more polarized, it also decreases.

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