Theoretical Study of Reactions with Electrophiles Substitutions: by B3lyp-Dft Density Function Calculation

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ABSTRACT
   Density functional theory (DFT), using the B3LYP functional was utilized to study the molecular properties (benzene molecule was a reference) of 1,3,5-Trihydroxybenzene (THB) compound in order to determine the relationship between molecular structure and electrophiles substitutions (nitration) efficiencies to get 2-nitro 1,3,5-Trihydroxybenzene (NTHB), 2,4-Dinitro 1,3,5-Trihydroxybenzene (DNTHB) and 2,4,6-Trinitro 1,3,5-Trihydroxybenzene (TNTHB) respectively. The best geometry for all molecules was investigated at (6-31G) basis sets. The total energies, ionization potentials, electron affinities, energy gaps, hardness and softness were calculated for the studied molecules. The electronic properties for all molecules were investigated by Gaussian (03) program.

Keywords: DFT, Electrophones Substitution, Nitration, Molecular Properties.

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دراسة نظرية للتفاعلات الباحثة عن الالكترنات بواسطة حسابات الدالة B₃L₄P-DF

الخلاصة

   استخدمت نظرية دالة الكثافة (DFT) عند المستوى G31-6 / B3LYP لدراسة الصفات الجزيئية للمركب 3،2،1- ثلاثي هيدروكسي بنزين (باستعمال جزيئة البنزين كمرجع)، لغرض تعيين العلاقة بين التركيب الجزيئي وفعالية التعويضات الباحثة عن الالكترونات (النيترة) للحصول على المركبات 2- نايترو 3،2،1- ثلاثي هيدروكسي بنزين (NTHB)، 2 ، 4 - ثنائي نايترو 3،2،1- ثلاثي هيدروكسي بنزين (DNTHB) و 2 ،4، 6- ثلاثي نايترو 3،2،1- ثلاثي هيدروكسي بنزين (TNTHB) بالتتابع. تم التاكد من افضل شكل هندسي باستعمال الدالة (G31-6). تم حساب الطاقات الكلية ، جهد التاين ، الالفة الالكترونية ، فجوات الطاقة ، الصلادة والليونة للجزيئات المدروسة. الصفات الالكترونية لجميع المركبات المدروسة تم تفسيرها حسب برنامج كاوسين (03).

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INTRODUCTION

Nitration is important for two reasons: firstly, because it is the most general process for the preparation of aromatic nitro compounds; secondly, because of the part which it has played in the development of theoretical organic chemistry. It is of interest because of its own characteristics as an electrophonic substitution [1].

Electrophilic nitration of aromatics is a fundamental reaction of great industrial importance, whose products are key organic intermediates or energetic materials. The nitration process has long been carried out using nitric and sulfuric acids (mixed acid) on a large-volume scale. For an increased emphasis on the topic of "green" chemistry and chemical processes, there is continuing concern regarding production of nitro compounds in the gas phase or by an alternative green synthetic strategy over chemical wastes and acidic drainage arising therefore. Since the classic studies by Ingold and his collaborators, it has been generally accepted that the nitrating agent is usually the nitronium ion, (NO_2^+), and that the reaction involves an intermediate σ-complex, called Wheland intermediate [2,3]. Despite the huge body of data that has been accumulated, the mechanism of aromatic nitration continues to be the subject of active research and some controversy [4-6].

Density function theory is one of the largest popular and successful quantum mechanical approaches [7]. It is a powerful computational quantum physical and chemical technique method that allows the calculation of the geometries and energies of reactants [8]. It has become a popular tool for electronic structure calculations in recent years due to its favorable combination of low computational cost and good accuracy for the calculated results. In analogy with wave mechanics methods, there are two main parameters controlling the accuracy of the results [9, 10].

Moreover, nowadays, computational chemistry methods offer a unique ability for the synthetic organic chemists to generate optimal geometry structures, and thought the structural and electronic properties of reactants and products make decisions as to which of the chemical transformations will occur in reactions. It was demonstrated that the B3LYP Density functional theory (DFT) is a reliable method for the calculation of geometries and energies [11, 12].

From the experimental there are some kinetic, and quantum mechanics studies of the reactivity of 1,3,5-Trimethoxybenzene that reports the qualitative prediction of reactive sites of those compounds [13].The optimized geometries and calculated electron density parameters of 1,3,5-Trihydroxybenzene was estimated in order to determinate their reactivity in electrophonic substitution (nitration) reactions. The differences in the stability were explained in terms of aromaticity and delocalization of electron densities on π molecular orbitals.

COMPUTATIONAL DETAILS

Calculations were done using the Density Functional Theory (DFT) method implemented in the Gaussian 03 suite of programs [14] with the B3LYP functional using the 6-31G basis set [15]. DFT/B3LYP combination is known to produce good estimate of molecular properties related to molecular reactivity [16]. Figure (1) represents the optimized geometries of the studied molecules, together with the HOMO and the LUMO respectively. Among the molecular properties that are well reproduced by the DFT/B3LYP method include the energy of the highest occupied

molecular orbital (HOMO), energy of the lowest unoccupied molecular orbital (LUMO), electron affinity (EA), ionization potential (IP), energy gap (Eg) electro negativity (X), global hardness (η) and softness (S), global electrophility index (ω).

According to Koopmans' theorem [17], the electron affinity ionization potential and electro negativity, may be defined in terms of the energy of the HOMO, the energy of the LUMO, global hardness and softness and global electrophilicity index.

Electron affinity is defined as the energy released when a proton is added to a system. It is related to E_{LUMO} through the equation:

$EA = - E_{LUMO}$

Ionization potential is defined as the amount of energy required to remove an electron from a molecule [18]. It is related to the energy of the E_{HOMO} through the equation:

$IP = - E_{HOMO}$

Energy gap generally refers to energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) according to the Koopmans theorem [19, 20]

$Eg = E_{LUMO} - E_{HOMO}$

Electronegativity is the measure of the power of an electron or group of atoms to attract electrons towards it [19, 21]; it can be estimated by using the equation:

$X = -1/2 (E_{HOMO} + E_{LUMO}) = 1/2 (IP + EA)$

It is evident that the aromaticity correlates with the thermodynamic stability of the system. There is also relationship between hardness and stability. Parr and Pearson [22, 23] reported the principle of maximum hardness: a rule that molecules arrange themselves to be as hard as possible. DFT method provides definitions of important universal concepts of molecular structure and reactivity. It was developed [24, 25] an operational approximation for absolute hardness:

$\eta = -1/2 (E_{HOMO} - E_{LUMO}) = 1/2 (IP - EA)$

Chemical softness is the measure of the capacity of an atom or group of atoms to receive electrons [26], it is estimated by using the equation:

$S = 1/ 2\eta = - 2/ (E_{HOMO} - E_{LUMO})$

The global electrophility index was introduced by Parr [25] and calculated using the electronagativity *and* chemical hardness parameters through the equation: $\omega = X^2/2\eta$

RESULTS AND DISCUSSION
Energies

Table (1) shows the values of the total energy and electronic states for the analyzed structures and the energy gap (Eg) of the studied molecules. The total energy for all study molecules as a linear function of (-OH and -NO$_2$) side group number adding to the molecule.

The total energy for all molecules is decrease with the addition of substitution groups, this give that molecule becomes more stable with increasing of group, this refer to that the total energy is dependent on the position and number of the (-NO$_2$) groups in the ring, especially when groups are nitro (electron with drawing), causes decreasing the HOMO and LUMO energy [27].

The energy gaps decreased are less than that of the original molecules. Therefore, the presence of substituent decreases the energy gaps improves the semi conductivities and also enhances the solubility's of these molecules, with decreasing

energy gap; electrons can be easily excited from the ground state. This effect of the side group was the largest in molecule NTHB it has energy gap of (3.47054 eV).

Table (1) show also the symmetry of study molecules, the benzene molecule (B) is planar with inversion center and have D_6h symmetry (high symmetry), molecules THB and DNTHB have same symmetry (Cs), while molecules B and NTHB have (C_1) symmetry.

Gipps energy (ΔG) was calculated according to following equation:

$$\Delta G = \Delta H - T\Delta S$$

Where ΔH = enthalpy of reaction (enthalpies of products - enthalpies of reactants), ΔS = entropy of reaction (entropies of products - entropies of reactants). All results of nitro compounds studies are positive charge and the values decrease when increase nitro clusters substitution in the ring.

Figure (2) shows the relationship between total energy, energies of HOMO and LUMO and energy gaps with number of molecules per unit (eV).
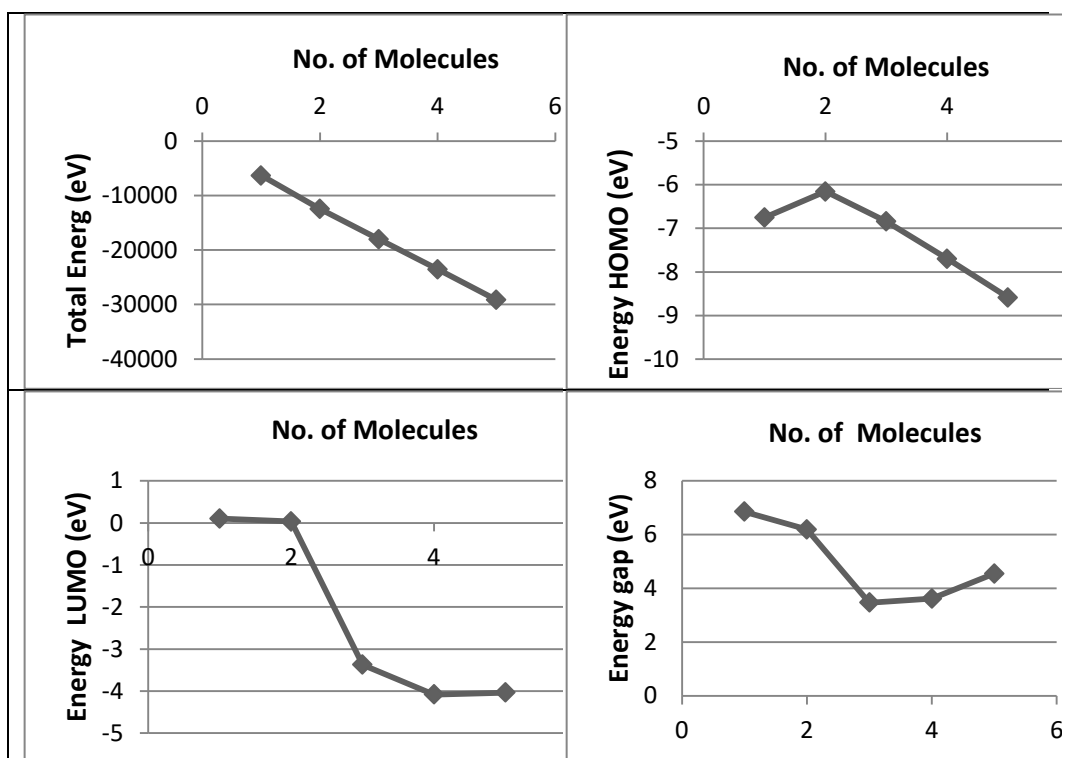

Figure (2) Energies per unit eV corresponding the NO. of molecules.

The energy gap is to be lowered from 6.85 eV of B to 3.61 eV for DNTHB as show in Figure (2) this is one of important results obtained in this study, DNTHB may indicated a new electronic material, in which it has smaller gap energy than B and other studied molecules, small energy gap means small excitation energies of manifold of the excited states.

Some important variables

B3LYP functional used in this study has a high efficient to calculate the electronic properties for the organic studied molecules, such as ionization

potentials(IP), electron affinities(EA), electro negativity (X), absolute hardness(η), absolute softness (S) and electrophonic index (ω). The properties are displayed in Table (2) lists the electronic properties for the molecules under study. It is clear from Table (2) that the ionization potential for THB molecule is lower than that for B but after adding the ($-NO_2$) cluster in the THB ring, have that the IP is larger than for B.

The electron affinity for THB group is less than that the electron affinity for B while after adding the ($-NO_2$) cluster to THB ring the electron affinities increase, especially for DNTHB ,these results mean that these molecules are more reactive and may be a signal to new states of material. It is obvious from this table that all molecules under study have hardness less than that for benzene. The behavior of electro negativity in the nitro molecules are largest from B, (softness and electrophlicity) index for the studied molecules shows the magnitude large than these for the original ring (benzene), adding the ($-NO_2$) cluster give the molecule more softness, it is a new electronic material.

Table (2) Computed energies for benzene, 1, 3, 5-Trihydroxybenzene and its nitro derivatives discussed in this work.

Number of Molecules	Symbols (Stoichiometry)	IP (eV)	EA (eV)	X (eV)	η (eV)	S (eV)$^{-1}$	ω (eV)
1	B (C_6H_6)	6.7511	- 0.1006	3.3252	3.4258	0.1459	1.6132
2	THB ($C_6H_6O_3$)	6.1554	- 0.0326	3.0940	3.0951	0.1615	1.5460
3	NTHB ($C_6H_5NO_5$)	6.8409	3.3714	5.1061	1.7347	0.2882	7.5140
4	DNTHB ($C_6H_4N_2O_7$)	7.6953	4.0789	5.8871	1.8082	0.2765	9.5839
5	TNTHB ($C_6H_3N_3O_9$)	8.5824	4.0327	6.3075	2.2748	0.2197	8.7406

CONCLUSIONS

A theoretical study of the stability and reactivity was carried out at the density functional theory calculation level for the structures of 1, 3, 5-Trihydroxybenzene and their nitro derivatives compared to benzene as reference. In general calculated values of IP, EA, Eg, X, η, S *and ω* were calculated and conclude that:

1. The density functional theory is a powerful method three parameters Lee-Yang-Par (B3LYP) functional is a suitable and an efficient function for studying the electronic properties of aromatic structures.
2. The total energies for THB found dependent on the position of the nitro cluster in the ring. Decreasing of the total energy with increasing the number of nitro groups refer to more stable substitution study molecules than benzene.
3. Studied molecules have high ionization potential and high electron affinity compared with benzene especially when increase of nitro groups in ring.
4. The geometric structures, symmetry and total energies for benzene and their studied molecules are in a good agreement with those in other references. But

for other molecules they have not been found similar studies, thus this study supplies new data in this aspect.

5. The hardness for all studied molecules group is lowers values in compare with benzene.

6. The electrophilicity increases when adding the nitro groups and it is still the good descriptor which may predict the reactive molecules with other atoms, molecules, and groups. The electrophilicity is high increasing from (8.74) eV for TNTHB to (9.58) eV for DNTHB.

7. Energy gap is a useful global property, soft molecules with small energy gap, their electron density change more easily than hard molecule. The presence of the nitro substituent decreases the energy gap of the molecules study; this is one of the important properties obtained in this work, NTHB molecule has lowest energy gap (3.46) eV.
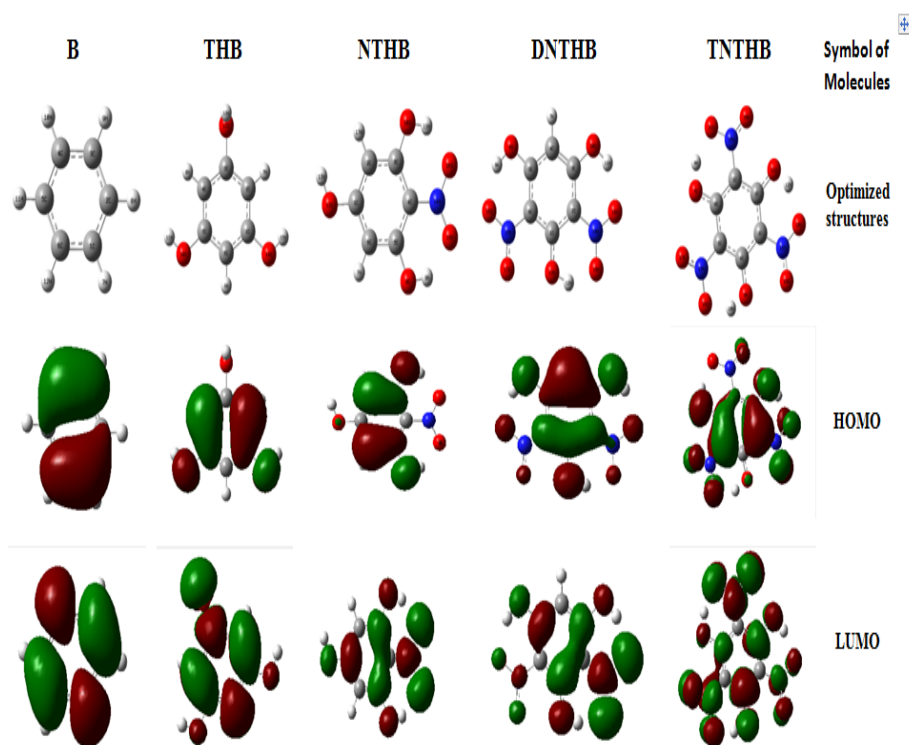

Figure (1) Optimized structures, HOMO and LUMO for the Studied compounds (B3LYP/6 -31G).

Table (1) Molecular mass, enthalpy, entropy, Gipps energy, Total energy, symmetry, electronic states and energy gap for Molecules under study.

No	Molecules symbol, (Stoichiometry), Name	Molecular mass (amu)	Enthlpy Kcal/mol (H)	Entropy Cal/Mol-Kelvin (S)	Gipps Energy Kcal/mol (ΔG)	Total Energy a.u (eV)	Symmetry	Electronic States a.u (eV)		Energy Gaps a.u (eV)
								HOMO	LUMO	
1	B (C_6H_6) Benzene	78.0469	66.586	68.790	-	-232.1987 (-6318.4517)	D_6h	-0.2481 (-6.7511)	0.0037 (0.1006)	0.2518 (6.8517)
2	THB ($C_6H_6O_3$) 1,3,5-Trihydroxy benzene	126.0316	74.565	84.406	-	-457.7602 (-12456.2959)	C_S	-0.2262 (-6.1552)	0.0012 (0.0326)	0.2274 (6.1878)
3	NTHB ($C_6H_5NO_5$) 2-Nitro 1,3,5 - Trihydroxy benzene	171.0167	78.496	94.866	3.3322	-662.2072 (-18019.5850)	C_1	-0.2514 (-6.8409)	-0.1239 (-3.3714)	0.1275 (3.4695)
4	DNTHB ($C_6H_4N_2O_7$) 2,4-Dinitro 1,3,5-Trihydroxy benzene	216.0018	80.782	108.853	0.6365	-866.6184 (-23581.899)	C_S	-0.2828 (-7.6953)	-0.1499 (-4.0789)	0.1329 (3.6164)
5	TNTHB ($C_6H_3N_3O_9$) 2,4,6-Trinitro 1,3,5-Trihydroxy benzene	260.9869	82.616	122.890	0.1693	-1071.0055 (-29143.559)	C_1	-0.3154 (-8.5824)	-0.1482 (-4.0327)	0.1672 (4.5497)

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