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THEORETICAL STUDY ON THE NITRATION OF *O*-PHENYLENEDIAMINE BY DENSITY FUNCTIONAL THEORY (DFT)

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ABSTRACT

In this study nitration (electrophilicity) affinities were calculated at all reactive positions of O-phenylenediamine (OPDA) in aromatic substitutions (electrophilic). Structures of products were optimized at B3LYP/6-31G level of theory. This was used in order to determine the effect of substituent (-NO_2) on the stability, reactivity and other properties of the O-phenylenediamine. From the calculated values of total energy, higher occupied molecular orbital (HOMO), lower unoccupied molecular orbital (LUMO), energy gap (Egap), electrophilicity (ω), electronegativity (x), hardness (η), softness (S) obtained, it can be inferred that 2,3,4,5-Tetranitro O-phenylenediamine is more stable and less reactive than other calculated compounds..

Keywords: *Nitration, O-phenylenediamine, Energy, Molecular Orbital, Stability, Reactivity, DFT.*

1. 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 electrophilic substitution [1].

The first nitration to be reported was that of benzene itself. Mitscherlich in 1834 prepared nitrobenzene by treating benzene with fuming nitric acid [2]. Not long afterwards the important method of effecting nitration with a mixture of nitric and sulphuric acids (mixed acid) was introduced, evidently in a patent by Mansfield [3]; the poor quality of early nitric acid was probably the reason why the method was developed. Since these beginnings, nitration has been the subject of continuous study. One of the characteristic properties of aromatic molecules is the ability to undergo substitution reactions with certain electrophiles [4]. This property has been used to decide whether a given molecule is aromatic or not. Electrophilic substitution is a manifestation of the tendency of an aromatic molecule to retain its cyclic conjugation system. When an electrophilicity attacks an aromatic molecule, it may enter into some specific positions in the molecule. However, it has not at all been clear whether or not an orientation in electrophilic substitution reflects aromaticity or extra substitution due to cyclic conjugation [5].

Aromatic nitration is a typical electrophilic substitution reaction, which is fully studied. For instance, the theory of electrophilic nitration proposed is considered a classic

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nitration reaction mechanism [6]. With the researches on reaction mechanism developed, other new nitrification theories such as self-nitrification and electron transfer are proposed [7, 8].

However, due to restriction of quantum computing models and methods, in particular, calculation conditions, there is some lack of knowledge about aromatic nitration mechanism of quantum chemistry exploration until recently [9].

Here, density functional method is used to calculate the physical properties between single and multiple electrophilic substitution reactions (nitration) of O-phenylenediamine (OPDA).

2. CALCULATIONS

All molecules geometries were fully optimized by Gaussian 03 program with B3LYP/DFT method and 6-31G level [10,11], structural optimization is done on all mono and multiple O-phenylenediamine (OPDA) substituted.

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

$$EA = - ELUMO \quad (1)$$

Ionization potential is defined as the amount of energy required to remove an electron from a molecule [12]. It is related to the energy of the EHOMO through the equation:

$$IP = - EHOMO \quad (2)$$

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 [13,14].

$$Eg = ELUMO - EHOMO \quad (3)$$

Electronegativity is the measure of the power of an electron or group of atoms to attract electrons towards itself [13,15], it can be estimated by using the equation:

$$X = -1/2(EHOMO + ELUMO) \quad (4)$$

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 [16, 17] 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. Parr and Senet [16, 18] developed a process to calculate the approximate absolute hardness:

$$\eta = -1/2 (EHOMO - ELUMO) \quad (5)$$

Chemical softness is the measure of the capacity of an atom or group of atoms to receive electrons [19], it is estimated by using the equation:

$$S = 1/ \eta \quad (6)$$

The global electrophilicity index was introduced by Parr [18] and calculated using the electronagativity and chemical hardness parameters through the equation:

$$\omega = X2 / (2\eta) \quad (7)$$

3. RESULTS AND DISCUSSION

3.1. ENERGIES

Table 1 shows the values of the enthalpy, entropy, Gipps free energy of reaction, total energy and symmetry for the analyzed structures. The total energy of all the molecules studied increases linearly with the addition of substitution groups ($-NO_2$). This give that molecule becomes more stable with increasing of substitution groups especially in

molecular M10 (2-3-4-5-Tetranitro *O*-phenyl enediamine) which has the maximum value (-31578.60) eV. The result showed that the total energy is dependent on the numbers of the (-NO_2) groups in the ring, as shown in monosubstitution, molecules (M2, M3), disubstitutions, molecules (M4, M5, M6, M7) and trisubstitutions, molecules (M8, M9).

The less total energy found in M7 molecule, it is mean that the molecule less stability then other compounds because has two substituted positions which are rare occur with amine groups.

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

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

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 studied were positively charged (endothermic reaction) and the values increase with increase nitro clusters substitution in the ring, and the values are stay in the same level when keep same number of nitro groups, the largest value found in C10 molecule.

When groups are nitro (electron withdrawing), causes increase the HOMO and LUMO energy (except M7 molecule). The energy gap decreased are less than that of the original molecules. Therefore, the presence of substituent decreases the energy gaps improves the semiconductivities and also enhances the solubility's of these molecules, solubility increases with increasing polarity of the molecule (positive relationship), and at the same time, the solubility increases with decreasing energy gap (inverse relationship), with decreasing energy gap; electrons can be easily excited from the ground state. This effect of the side group was the largest in molecules (M3) which has energy gap (3.4670) eV.

The results in Table 2 shows that the electronegativity (X) in studied molecules were increased with increase nitro substitution, and stay same value in molecules which have same number of substitution groups (M2, M3), (M4, M5, M6),(M8, M9), the largest value found in (M10) molecule (5.9616) eV, the least value found in (M7) molecule (0.1198) eV.

Hardness values of studied molecules were less in all molecules compared with general molecular (M1); and (M10) molecule has highest value. While the result show increase in softness values in all studied molecules compared with molecular (M1). While softness values were increase with substitution group compared with (M1) molecule, and largest value was found in (M7) molecule.

The electrophilicity index (ω) were increased with increase groups of nitration, and M10 molecule has the maximum value (11.4000) eV, as shown in Table 2.

Figure 1 shows the relationship between total energy, energies of HOMO and LUMO and energy gap with number of molecules per unit (eV).

3.2. Quantitative calculation of C atoms' net charge on substituted *O*-phenylenediamine ring

By B3LYP/DFT method and 6-31G level [20, 21], structural optimization is done on all substituted *O*-phenylenediamine (OPDA) ring, and the net negative charge of each C atom is calculated particularly. All molecular structures are drawn in Fig. 2. The orientation effect of electrophilic aromatic substitution is described with the net charge of each atom. By B3LYP/6- 31G group, net charge of each C atom on *O*-phenylenediamine (OPDA) ring is calculated and shown in Table 3.

TABLE 1 : THE VALUES OF THE ENTHALPY, ENTROPY, GIPPS FREE ENERGY OF REACTION, AND TOTAL ENERGY FOR THE ANALYZED MOLECULES.

Symbols of Molecules	Structure Molecule	Enthlpy Kcal/mol (H)	Entropy Cal/Mol-Kelvin (S)	Gipps Free Energy KCal/Mol (ΔG)	Total Energy (eV)
M1	O-phenylene diamine (OPDA)	89.549	81.260	-	-9329.97
M2	3-nitro OPDA	92.513	93.104	1.952	-14892.80
M3	4-nitro OPDA	92.450	94.686	1.418	-14892.88
M4	3,4-dinitro OPDA	95.000	106.926	2.838	-20347.10
M5	3,5-dinitro OPDA	95.168	106.917	3.009	-20455.39
M6	3,6-dinitro OPDA	95.289	105.256	3.625	-20455.44
M7	4,5- dinitro OPDA	94.916	108.926	2.158	-751.6971
M8	3,4,5-Trinitro OPDA	97.419	120.251	3.804	-26016.7
M9	3,4,6-Trinitro OPDA	97.599	119.428	4.230	-26017.09
M10	3,4,5,6-Tetranitro OPDA	99.845	131.009	5.543	-31578.60

TABLE 2 : THE RESULTS OF HOMO, LUMO, ENERGY GAP, ELECTRONEGATIVITY, HARDNESS, SOFTNESS AND GLOBAL ELECTROPHILICITY INDEX OF ALL MOLECULES STUDIED, (IN EV).

Symbol	HOMO	LUMO	Egap	X	ɳ	S	ω
M1	-4.7601	0.6795	5.4396	2.0403	2.7198	0.3676	0.7652
M2	-5.6619	-2.4705	3.1914	4.0662	1.5957	0.6266	5.1807
M3	-5.7299	-2.2630	3.4670	3.9964	1.7334	0.5768	4.6068
M4	-6.3258	-3.1862	3.1397	4.7560	1.5698	0.6370	7.2045
M5	-6.5087	-3.1671	3.3416	4.8379	1.6708	0.5985	7.0042
M6	-6.3868	-3.5824	2.8044	4.9846	1.4022	0.7131	8.8597
M7	-0.2325	-0.1127	0.1198	0.1726	0.0599	16.694	0.2486
M8	-6.9593	-3.6491	3.3103	5.3042	1.6551	0.6041	8.4993
M9	-7.0124	-4.0368	2.9756	5.5246	1.4878	0.6721	10.2576
M10	-7.5204	-4.4028	3.1176	5.9616	1.5588	0.6415	11.4000

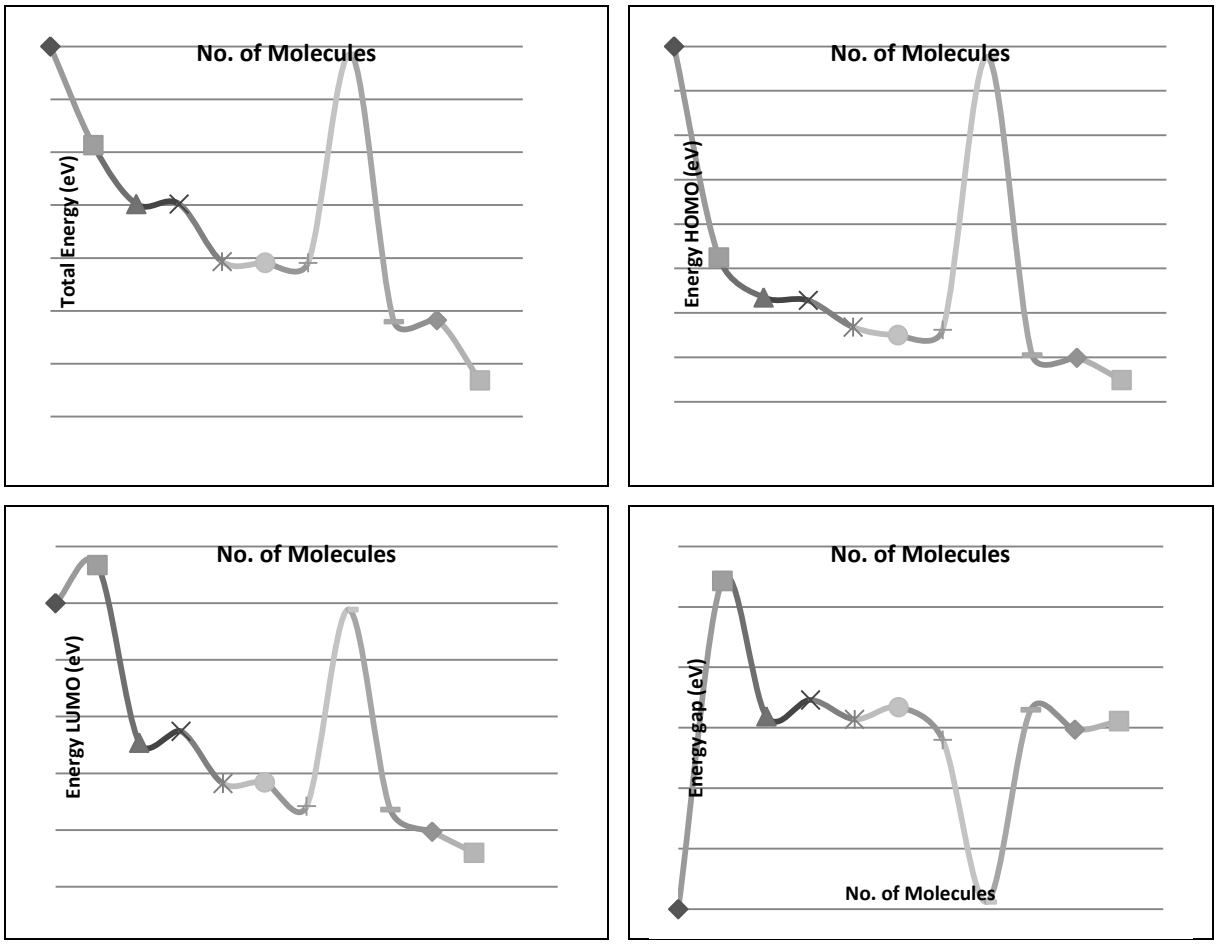

Fig.1. The relationship between total energy, HOMO, LUMO, and energy gap and molecules studied.

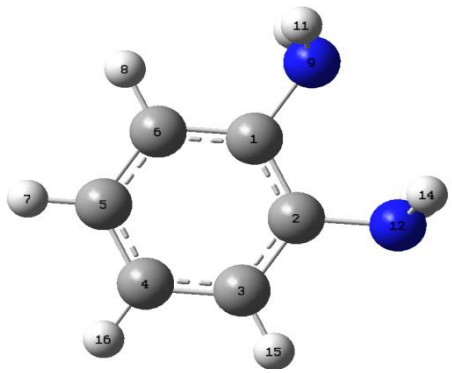

Fig.2. Molecular structure O-phenylenediamine (OPDA) draw by Gaussian view.

Underline numbers mean the best carbon atoms which substituted by nitro group.

From the mechanism, aromatic nitration is an electrophilicity reaction. For C3 - C6 on o-phenylenediamine ring, the C atom holding largest negative charge is the best position to nitro-substituted in, and its product should be the main component of the total products. If there is another C atom's negative charge close to the maximum value, substitution will also occur and the share of its product will depends on the approximate amount of negative charge compared with the maximum value, or the C atom's negative charge is far from the maximum value, the substitution products will not occur.

Analysis the data calculated : in *O*-phenylenediamine (M1), C3 and C6 positions' negative net charge is largest and closely, their products most likely to occur; with similar in M1 molecule, this main the first nitration probability occur on C3 or C6 position to get M2 molecule, more than that of C4 or C5

TABLE 3: NET CHARGE NUMBER OF C3 - C6 CARBON ATOMS IN *O*-PHENYLENEDIAMINE (OPDA) RING.

Molecules Symbol	Molecules	Net charge number of every carbon atom in *O*-phenylenediamine ring according to Figure (2)			
		C3	C4	C5	C6
M1	OPDA	-0.146	-0.136	-0.136	-0.146
M2	3-Nitro OPDA	+0.325	-0.124	-0.152	-0.116
M3	4-Nitro OPDA	-0.134	+0.311	-0.119	-0.164
M4	3,4-Dinitro OPDA	+0.344	+0.296	-0.123	-0.136
M5	3,5-Dinitro OPDA	+0.314	-0.118	+0.300	-0.105
M6	3,6-Dinitro OPDA	+0.358	-0.143	-0.143	+0.358
M7	4,5-Dinitro OPDA	-0.145	+0.322	+0.322	-0.145
M8	3,4,5-trinitro OPDA	+0.374	+0.276	+0.343	-0.127
M9	3,4,6-Trinitro OPDA	+0.361	+0.289	-0.125	+0.030
M10	3,4,5,6-Tetranitro OPDA	+.386	+0.291	+0.291	+0.386

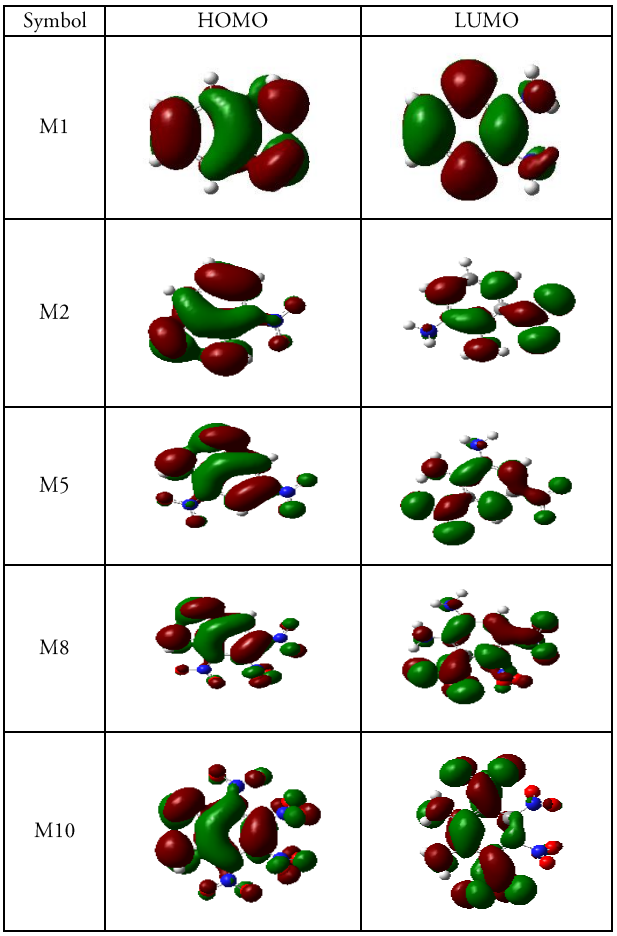

Fig.3. Optimized structures, HOMO, LUMO for (M1, M2, M5, M8, M10) molecules the studied compounds (B3LYP/6-31G).

position to get molecule M3. Therefore, we will get M2 molecule as a main product rather than M3 molecule.

The second nitration probability occur in the M2 molecule is on position C5 rather than C4 or C6 position, therefore we will get M5 molecule as main product, and M5 molecule has C4 position largest negative charge, therefore the third nitration will get M8 molecule as main product. Final nitration on M8 molecule will get M10 molecule by attack on last free position C6.

The frontier molecular orbital pictures of molecules under study (M1,M2,M5,M8 and M10) are shown in Fig.3 . We present only the HOMO and LUMO. The energy difference between the HOMO and LUMO for nitro compounds above is (3.3416 eV) for M5.

4. CONCLUSIONS

Evident from the results that have been obtained that the compound M10 is the most stable because has largest HOMO (-7.5204) eV, the most hardened (5.9616) and this is

evident to the fact that the compound may compensated all its positions with nitro groups, while the compound M7 is the least stable (has least value of HOMO (-0.2325) eV), and least hardness (0.1726) eV, while the M3 compound is the largest value energy gap compared with the rest of the compounds that was prepared.

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دراسة نظرية لنيترة الاورثوفنيلين ثنائي الامين باستخدام دالة الكثافة الالكترونية (DFT)

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الملخص:

في هذه الدراسة تم حساب النيترة (التفاعلات المحبة للألكترون) في جميع المواقع الفعالة للتعويضات على حلقة المركب الاورثوفنيلين ثنائي الامين ؛ تم حساب تركيب النواتج عند المستوى النظري B3LYP/6-31G. استخدم ذلك لتعيين تاثير التعويض بمجاميع النيتور (-NO2) على الاستقرارية ، الفعالية وبقية الصفات للمركب الاورثوفنيلين ثنائي الامين . من القيم المحسوبة للطاقة الكلية ، طاقة اعلى اوربتال جزيئي محتل (HOMO) ,طاقة ادنى اوربتال جزيئي غيرمحتل (LUMO) ، فجوة الطاقة (Egap) ، الالفة الالكترونية (ω) ، السالبية الكهربائية (x) ، الصلادة (η) والليونة (S) ، يمكن الاستدلال ان المركب 2،3،4،5- رباعي نايترو الاورثوفنلين ثنائي الامين هو الاكثر استقرارا والاقل فعالية من بقية المركبات المحسوبة.