Density Functional Theory Calculations for Nitro Benzene Molecules Group

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Abstract
Electronic properties for nitrobenzene molecules have been studied using three parameters Lee-Yang-Parr density functional theory with 6-31G** basis sets. The optimized structures and electronic properties calculations for the studied molecules have been performed using Gaussian 03 program. This study includes benzene molecule calculations for comparison and study the addition effect of nitro as a side group on the electronic properties of benzene. The results show that the energy gaps for nitrobenzene molecules group is less than that for benzene.

Keywords: DFT, Ionization potential, electron affinity, energy gap, and IR spectrum.

Introduction

Aromatic compounds are important in industry and play key roles in the biochemistry of all living things [1], nitro-substituted on aromatic molecules are members of a class of environmental contaminants found in airborne particulate matter, fossil fuel combustion products, coal fly ash, cigarette smoke, and vehicular emissions, formed by reactions of aromatic molecules with nitrogen oxide [2]. There are many organic materials show useful field effect transistor performance, which can be characterized by their carrier mobility and on/off current ratios [3, 4]. Many studies on cyclic oligomers have been reported both experimentally and theoretically [5, 6], in [7] the substituent effects of oligomers such as oligothiophene, oligopyrrole and oligofuran are discussed in terms of reorganization energy. Also, [8] studied the geometric and electronic properties for cynothiophene oligomers as a prototype of an organic conducting polymer using ab initio and DFT [9], they showed that the cyno group generally reduced the band gap with variation of the substitution position.
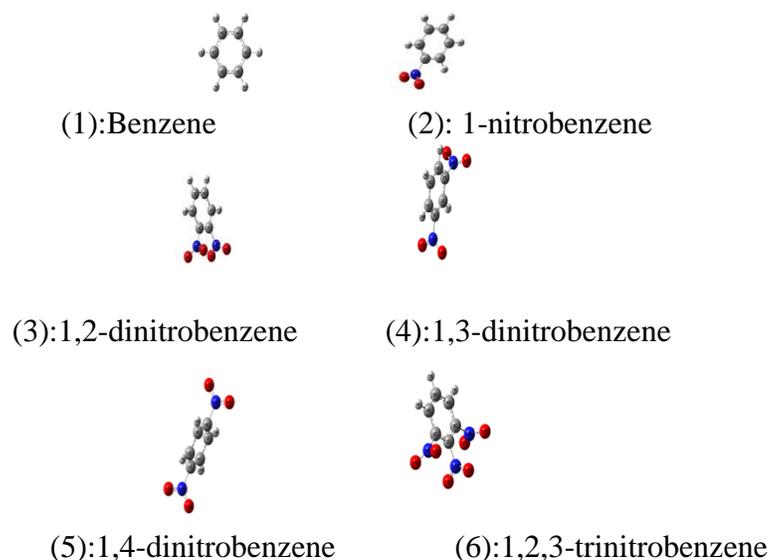
Nitrobenzene molecules group are aromatic compounds possesing the ring structure of benzene or other molecular structures that resemble benzene in electronic configuration and chemical behavior. These compounds are manufactured on a large scale for use in high octane gasolines and in the production of polymers, insecticides, detergents, dyes and many miscellaneous chemicals[10]. There are many compounds that, at first appearance, bear little resemblance to benzene, but have a basic similarity in electronic configuration, and they are aromatic, too[11, 12]. Benzene was formed from a six membered carbon ring with alternating single and double bonds, was developed by Kekule [13]. The model for benzene consists of two resonance forms, which corresponds to the double and single bonds switching positions[14].

In present work, density functional theory has been performed to study the electronic properties of the nitrobenzene molecules to determine the effects of the substituent groups and evaluation of their infrared spectrum.

Computational details

Figure 1 represents the molecules under study. All the computational studies were carried out using the density functional theory (DFT) methods implemented in the Gaussian 03 suite of programs [15]. The molecular properties of the compounds have been computed by DFT using the standard 6-31G(d, p) basis sets. In the DFT calculations the Lee, Yang and Parr correlation functional [16] is used together with Becke's three parameters [17] exchange functional B3LYP. Conformational analysis of the molecules has been performed to have an idea about the lowest energy structures of the species.

The geometry optimization was performed at the B3LYP density functional theory with the same basis sets [16,18]. Harmonic vibrational frequencies were computed at the same level of theory. The hybrid functional B3LYP has shown to be highly successful for calculation the electronic properties such as ionization potentials, electronic states and energy gaps [19-21].The DFT partitions the electronic energy as $E = E_T + E_V + E_J + E_{XC}$, where E_T, E_V and E_J are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms, respectively. The electron correlation is taken into account in DFT via the exchange correlation term E_{XC}, which includes the exchange energy arising from the antisymmetry of the quantum mechanical wavefunction and the dynamic correlation in the motion of individual electrons; it makes DFT dominant over the conventional HF procedure [22]. The geometry optimized structures are obtained by restricted closed-shell formalism and without any symmetry restriction, and vibrational analysis for some structures does not yield any imaginary frequencies, which indicates that these structures of the molecules correspond to at least a local minimum on the potential energy surface [23].
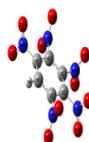

(1):Benzene   (2): 1-nitrobenzene

(3):1,2-dinitrobenzene   (4):1,3-dinitrobenzene

(5):1,4-dinitrobenzene   (6):1,2,3-trinitrobenzene
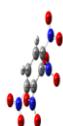
(7):1,3,5-nitrobenzene   (8):1,2,3,4-tetranitrobenzene

(9): 1,2,3,4,5-pentanitrobenzene

Figure 1. Optimized Structures of benzene and its derivatives discussed in this work. In this investigation, the more relevant electronic potential (IP), electron affinities (EA), chemical potential (μ) it is the negative of electronegativity (χ), hardness (η), softness (S), electrophilic index (ω) and the electric dipole polarizability (α) were calculated. The HOMO and LUMO energy was used to estimate the IP and EA in the framework of Koopmans' theorem[24]: $IP = -\varepsilon_{HOMO}$ and $EA = -\varepsilon_{LUMO}$

 Within the framework of the density functional theory (DFT), one of the global quantities is Within the framework of the density functional theory (DFT), one of the global quantities is chemical potential (μ), which is measures the escaping tendency of an electronic cloud, and equals the slope of the Energy versus N(number of electrons) curve at external potential v(r) [25]:

$$\mu = \left[\frac{\partial E}{\partial N}\right]_{v(r)} \qquad (1)$$

 Finite difference approximation to Chemical Potential gives,

$$\mu \approx -\chi = -(IP + EA)/2 \qquad (2)$$

The theoretical definition of chemical hardness has been provided by the density functional theory as the second derivative of electronic energy with respect to the number of electrons N, for a constant external potential v(r) [25]: $\eta = \frac{1}{2}\left[\frac{\partial^2 E}{\partial N^2}\right]_{v(r)} = \frac{1}{2}\left[\frac{\partial \mu}{\partial N}\right]_{v(r)}$ (3)

Finite difference approximation to Chemical hardness gives,

$$\eta = (IP - EA)/2 \qquad (4)$$

For Insulator and semiconductor, hardness is half of the energy gap ($\varepsilon_{HOMO} - \varepsilon_{LUMO}$), and the softness is given as [24]: $S = \frac{1}{2\eta} = \left(\frac{\partial^2 N}{\partial E^2}\right)_{v(r)} = \left(\frac{\partial N}{\partial \mu}\right)_{v(r)}$ (5)

Electrophilicity index is a measure of energy lowering due to maximal electron flow between donor and acceptor. Electrophilicity index (ω) is defined as [22],

$$\omega = \frac{\mu^2}{2\eta} \qquad (6)$$

One of the other global properties is the electric dipole polarizability, which is a measure of the linear response of the electron density in the presence of an infinitesimal electric field, F, and represents a second-order variation in the energy, viz.[25] :

$$\alpha = -\left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right) \quad a,b = x, y, z \qquad (7)$$

If some of applied molecules are planar and some are not, it will be useful to report polarizability quantities that are invariant to the choice of coordinate system. One of them is the mean polarizability $< \alpha >$ is evaluated using the equation [22].

$$< \alpha > = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \qquad (8)$$

Where $\alpha_{xx} \leq \alpha_{yy} \leq \alpha_{zz}$ are the eigenvalues of the polarizability tensor.

Results and discussion
I. Symmetry and electronic states

The total energies, symmetry of structures electronic states and energy gaps for molecules calculated by DFT-B3LYP levels with the 6-31G(d, p) basis set are listed in table 1.

Table 1: Energy, symmetry , electronic states and energy gap for molecules

Mol.	Energy(au)	Symmetry	Electronic State (ev)		Energy gap
			homo	lumo	
1	-232.27788	D_{8h}	-7.03242	-0.45957	6.57285
2	-436.7932	C_{2v}	-7.56465	-2.45162	5.11303
3	-641.2962	C_{2v}	-8.08817	-2.9735	5.11467
4	-641.3031	C_{2v}	-8.11238	-2.97813	5.13425
5	-641.304	D_{2h}	-8.01497	-2.91527	5.0997
6	-845.808	C_{2h}	-8.68842	-3.77048	4.91794
7	-845.8083	C_{3h}	-8.68461	-3.39091	5.2937
8	-1050.3066	C_2	-9.10718	-4.47876	4.62842
9	-1254.8031	C_s	-9.46282	-4.8197	4.64312

Table (1) shows that the total energy for all studied molecules as a linear function of NO_2 side group number adding to the molecule. The final total energy of the product is the collection of total energy of all small molecules which build the product molecule, that means:

$$E_{tot} \approx E_{tot}(benzene) + nE_{tot}(NO_2) \qquad (9)$$

Where n is the number of NO_2 radicals.

It is clear that from Table 1, the total energy for all dinitrobenzene molecules is approximately the same, also it is approximately the same for all tri-nitrobenzene molecules in
which this refer to that the total energy depends on the number of radicals added to the ring and independent on the position of the nitro radical in the ring, and it is observed that substitution of nitro groups causes decreasing the HOMO and LUMO energy, it is known that the electron with drawing substituent reduce the LUMO and HOMO energies [26,27],

and energy gap decreased. Therefore, the presence of substituent decreases the energy gaps improves the conductivities and also enhances the solubility of these molecules. The LUMO-HOMO energy gaps of nitrobenzene molecules is less than that of the original molecule, with decreasing energy gap, electrons can be easily excited from the ground state [28,29]. This effect of the side group was the largest in molecule **9** it has energy gap of (4.643 eV). The energy gap of benzene (6.572 eV) is agreements with experiment value (6.67 eV). The table 1 shows also the symmetry of studied molecules, the molecule **1** is planar with inversion center and have D_{6h} symmetry (high symmetry), and have lower electronegativity, while molecule **9** is planer and have C_S symmetry (low symmetry), and have higher electronegativity.

II. Some electronic properties

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), electronegativity (χ), absolute hardness (η), absolute softness (S), electrophilic index (ω). The properties that are displayed in Table 2 for each variable are computed based on the differences between the HOMO and the LUMO energies of the neutral molecule and is known as orbital-vertical (Koopmans' theorem).

Table 2 : The electronic properties of nitrobenzene molecules group from DFT

Mol.	IP (eV)	EA (eV)	χ (eV)	η (eV)	S /(eV)	ω (eV)
1	7.03242	0.45957	3.745995	3.286425	0.152141	2.134915
2	7.56465	2.45162	5.008135	2.556515	0.195579	4.905392
3	8.08817	2.9735	5.530835	2.557335	0.195516	5.980862
4	8.11238	2.97813	5.545255	2.567125	0.19477	5.989162
5	8.01497	2.91527	5.46512	2.54985	0.19609	5.856724
6	8.68842	3.77048	6.22945	2.45897	0.203337	7.890712
7	8.68461	3.39091	6.03776	2.64685	0.188904	6.886402
8	9.10718	4.47876	6.79297	2.31421	0.216056	9.969804
9	9.46282	4.8197	7.14126	2.32156	0.215372	10.98348

The calculated properties for each variable as shown in Table 2 clearly reveal that these nitrobenzene molecules have a tendency to capture electrons instead of donating them. The ionization potential for the nitrobenzene molecules group is greater than that for the original molecule, but the penta-nitrobenzene molecule has the largest value of ionization potential, this indicates that this molecule needs high energy to become cation comparing with the others. The strength of an acceptor molecule is measured by its electron affinity (EA) which the energy released when adding one electron to LUMO. An acceptor must have a high EA, adding the radical to the ring leads to increasing the ability of the electron affinity for the molecule, EA for molecule **9** is the largest, as we see in Table 2. The calculation value of IP, EA and energy gaps for molecule **1** is a good agreement with experimental value [30-32].

Few interesting observations have been made from the results that are shown in Table 2 obtained through the orbital-vertical method. The electron affinities (EA) computed from the energy of the lowest unoccupied molecular orbital (LUMO) are higher for all studied molecules than that of the original molecule. From the previous investigations, it has been found that for almost all the commonly used exchange-correlation functional such as

B3LYP, B3PW91, Koopmans's theorem is satisfy accurately . The two results obtained by the calculation of electronegativity and electrophilicities also agreed very well with the employing method for these molecules. This could be the reason for the low hardness values obtained from this method. Therefore, the Koopmans's theorem is a best useful and fast approach [30]. The behavior of electronegativity, softness and electrophonic index for the studied molecules shows the magnitude large than these for the original ring, adding the radicals give the molecule more softness. The molecules dipole moment represents a generalized measure of bond properties and charge densities in a molecule [30]. Molecule with electron accepter group due to better charge distribution and increasing distance have higher dipole moment[25], from Table 3 molecule **6** has higher dipole moment (6.982 Debye).The results of the calculated polarizability for (**1** – **9**) molecules in table 3 showed that all substitution groups leads to increase the average polarizability and cause more reactive than the original (molecule **1**). The molecules **8** and **9** have average dipole polarizability equal 141.630 and 161.416 a.u, they have the highest polarizability and have highest reactivity. This due to the ring delocalizing π electron resonance from the phenyl groups [25].

Table 3: calculated total dipole moment μ (Debye), components of α_i (i = xx, yy, zz) and average of the dipole polarizability $< \alpha >$ in (a u) for studied molecules.

| Mol.	μ	α_{xx}	α_{yy}	α_{zz}	$< \alpha >$
1	0.000	81.403	81.400	44.740	69.181
2	4.128	107.929	86.306	63.609	85.948
3	6.396	121.261	104.606	81.372	102.413
4	3.889	126.224	101.629	82.835	103.562
5	0.0002	137.072	91.243	82.924	103.746
6	6.982	149.593	140.419	78.978	122.996
7	0.0070	132.282	132.217	102.137	122.212
8	5.426	175.349	153.915	95.627	141.630
9	2.538	195.626	179.694	108.928	161.416

III. IR Spectra

The IR spectra of (**1**- **8**) molecules are provided in fig. (2). The harmonic vibration frequencies calculated for studied molecules at B3LYP level using the 6-31G(d, p) basis sets. The (C – H) stretching vibrations of aromatic molecules in the region (2900 – 3250) cm^{-1} which is characteristic region for ready identification of (C – H) stretching vibrations and particularly the region (3250 – 3100) cm^{-1} for asymmetric stretching and (3100 – 2900) cm^{-1} for symmetric stretching modes of vibration [30].

The present work gives the frequency values at (691, 1066.3, 1528.28 and 3202.34)cm^{-1} for benzene which are consistent with experimental results of (673, 1038 , 1469 , and 3210)cm^{-1}, and the aromatic molecules frequency has both in-plane (1100 – 1700) cm^{-1} and out-of-plane (below 1000 cm^{-1})(C – H) bending vibrations, the in-plane vibration for benzene calculated at 691cm^{-1}, 1066.3cm^{-1} which a good agreement with experimental results 673cm^{-1} and 1038cm^{-1}[39].

It is clear from fig. (2) that the IR spectrum for nitrobenzene molecules characters from that of benzene by multiply the vibration mode due to existing of (N – O) , (C – N)

bonds, (C = C) stretching and (C − H) stretching, for (**2 − 9**) molecules the stretching of (C − N) bond has been observed at (1215 − 1490) cm^{-1} , the (C − H) stretching stay in the region (3100 − 3210) cm^{-1}, the stretching of (C − N) bond has been observed at (1215 − 1490) cm^{-1} and the stretching of (C = C) bond at the range (1200 − 1700) cm^{-1},while the bending of (N − O) bond appeared at (1320 − 1700) cm^{-1}. The π electron density on the aromatic ring was delocalized the presence of the -NO$_2$, which reduced the strength of (C = C) bond and depending on the position of nitro group. The torsion vibrations appear at very low frequency for (**2 −9**) molecules at below 50 cm$^{-1.}$

Figure 2: The IR spectra of molecules under study, Epsilon = Intensity (Km/mol).

(1)

(2)

(3)

(4)

(5)

(6)

(8)

(7)
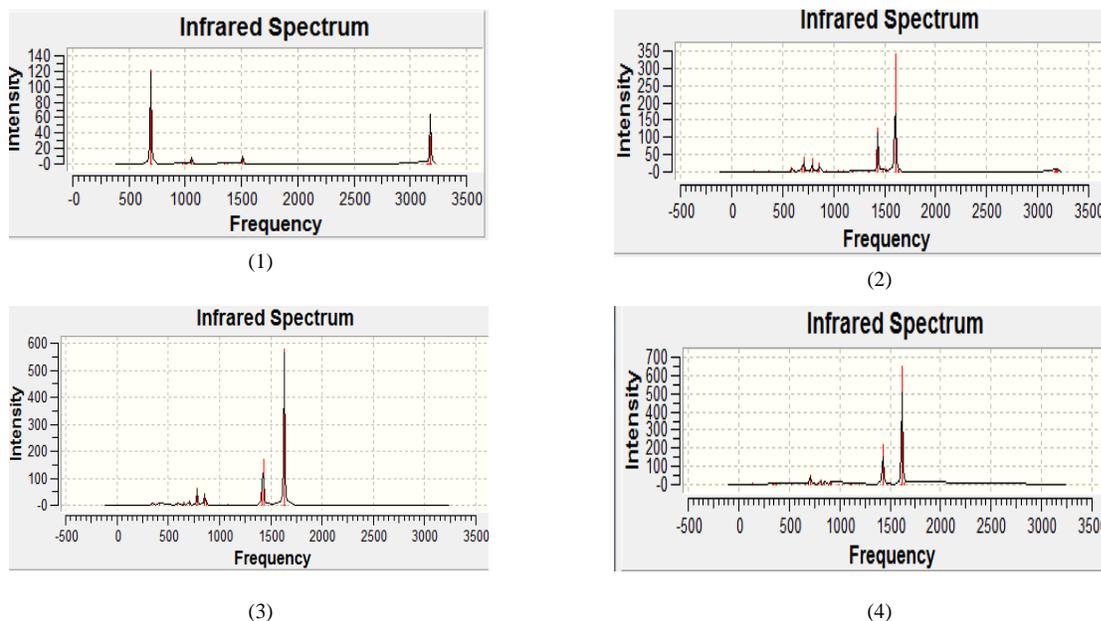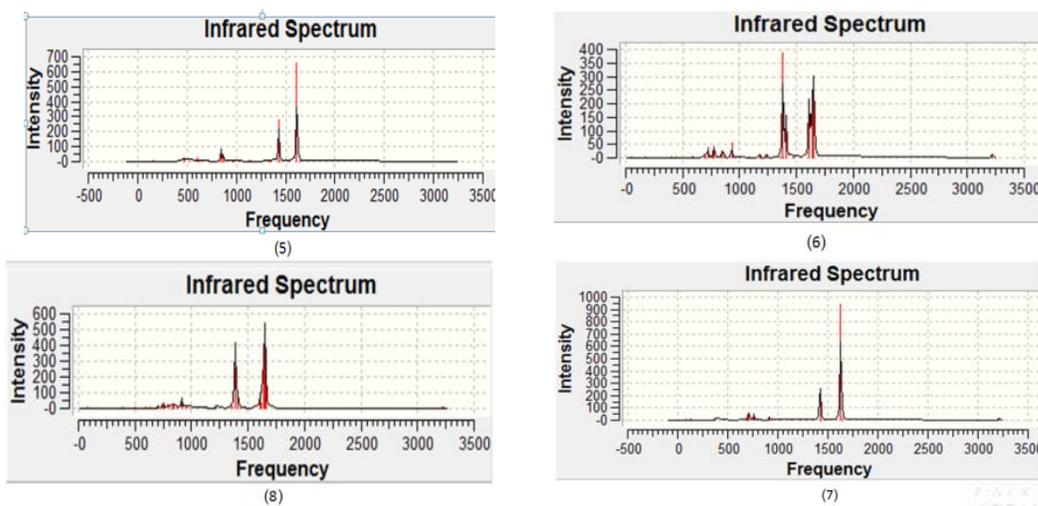
IV. Conclusions:

We have use DFT in this study to compute geometry optimization and electronic properties of benzene and nitrobenzene molecules group by using B3LYP function. The calculated electronic properties such as ionization potential, electron affinity, electro-negativity, hardness, softness and electrophilic index by using the orbital-vertical method, the important conclusions are:

1- Geometry optimization for molecule **1** has been found in a good agreement with experimental data, while for other studied molecules (**2** – **9**) it has not been found a reference data.

2- The total energies for dinitrobenzene and tri-nitrobenzene found not dependent on the position of the nitro radical in the ring and substitution nitro group causes decreasing energy and leads to more stability.

3- The presence of the substituent decreases the energy gap of the studied molecules, this is one of the important properties obtained in this work, and a small energy gap means small excitation energies of manifold of the exited states.

4- The electronic properties (IP, EA, χ, η, S, ω) was calculated by using B3LYP density functional method are in good agreement with experimental result and better than from other were calculated by other theoretical method.

5- The results showed that all substitution groups leads to increase the average polarizability and dipole moment and cause to more reactive than original molecules.

6- In IR spectra calculation shows a good agreement with experimental data for benzene (molecules **1**), adding the nitro groups leads to increasing the vibration modes, and highest stretching vibration wave numbers and its gave suitable positions for NO_2 with carbon atoms in phenyl ring.

7- Molecule **9** is the best option for n-type organic semiconductors because of its better HOMO – LUMO ratio and other electronic properties.

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