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Computational Calculation of Nitrobenzene and Its Derivatives

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Abstract

Nitrobenzene is one of benzene derivatives. Nitrobenzene can be found naturally and also from the synthesis process. Nitrobenzene is used as a raw material to synthesize aniline, textile dyes, pesticides, and drugs. Nitrobenzene is a solvent in the paint industry. The computational calculation was performed for nitrobenzene and its derivatives. Nitrobenzene and its four nitrobenzene derivatives have been optimized using density functional theory/B3LYP functional. The basis set is 3-21G(d). The optimized structure from geometry optimization of the nitrobenzene and its derivatives are in one plane (planar). The parameter structure is changed when substituents change. The bond length increases, and the bond angle decreases when substituents are present.

Keywords: Nitrobenzene, DFT, derivatives, bond length, 3-21G(d).

INTRODUCTION

Nitrobenzene is a derivative of benzene. Nitrobenzene is benzene bound to the NO_2- group. Nitrobenzene has derivatives and analogues. Nitrobenzene derivatives can be used as a reactant to synthesize other molecules. Alkyl nitrobenzene is one of nitrobenzene derivatives. It can be used to synthesize 3H-azepine compounds by a one-step thermal reaction (Ulfa et al., 2015).

The different substituents present in the compound can give different properties. Different structures can cause these different properties due to different molecular groups bonded directly to the primary molecule. The structure and properties of a compound can be known from computational calculations. The nitrobenzene structure is shown in Figure 1.

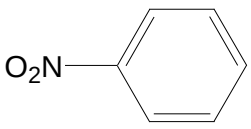


Figure 1. Nitrobenzene Structure

The potency of a molecule can be known through computational calculations. The computational chemistry calculations provide information in the form of the structure and electronic properties of the molecule. Maahury & Allo (2021) have optimized geometry of 1-aeroplysinin before using for molecular docking and obtained a stable structure for interaction as antibacterial. Muliadi, et al (2021) have done computational analyses for myristicin derivatives and established their properties as antioxidant compounds by QSAR. Computational calculations can also be helpful before any experimental work is carried out. Paramita et al. (2020) investigated 1,3,4-thiadiazole properties using semiempirical method before developing it experimentally. Chemical reactions can also be analyzed using computational calculations. Indarto & Handojo (2020) have analysis formation Mechanism of cyclic hydrocarbons from C_4H_5 and C_4H_2. The calculation results show that there is growth process mechanism more possible to happen compared with a polyne based process.

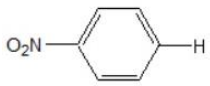
The stable structure and electronic properties of nitrobenzene and its derivatives can be reached by computational calculation. Nitrobenzene has been analyzed with computational calculation by Krishnakumar et al. (2016). They use the B3LYP functional DFT theory and the cc-pvDz basis set and get . Kumer et al. (2017) have calculated aniline and nitrobenzene using the DFT/ WB97XD and HF. Based on the computational calculation, the result gives good agreement about the presence of atoms in a molecule. Soto & Algarra (2021) have calculated the electronic structure of nitrobenzene to know the singlet and triplet vertical excitation energies using MS-CASPT2/CASSCF level with a functional reference space of twenty electrons distributed in seventeen orbitals. They get that nitrobenzene has five

singlet valences, which correspond to single excited configurations. Wang et al. (2016) have used DFT with the dispersion correction to investigate the structural properties of solid nitrobenzene at ambient pressure. They get that the DFT-D calculated results are a good complement to the experiments, which helps to understand the energetic molecular behavior of crystal nitrobenzene under high pressure.

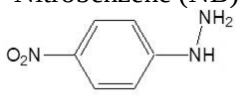
The computational calculation of nitrobenzene derivatives has been done. Makwani & Vijaya (2007) have used the ab-initio theory to calculate the first hyperpolarization of several benzene derivatives and find a good correlation between result from the experiment and calculation. In that calculation, they just used Hartree-Fock (HF) with 6-31G(d) basis set. There was no calculation of nitrobenzene derivative molecules from Makwani & Vijaya (2007) using DFT. So, this research carried out a calculation on nitrobenzene and its derivatives. There are five molecules; there are nitrobenzene, 1-(4-nitrophenyl) hydrazine (2), 4-nitrobenzamine (3), 1-methoxy-4-nitrobenzene (4), and N-ethyl-4-nitrobenzene. These four molecules calculated computationally using DFT theory with functional B3LYP/3-21G(d).

METHODOLOGY

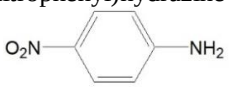
Nitrobenzene and its derivatives structure was built before the optimization. The structures were optimized using Density Functional Theory with B3LYP. The basis for this calculation is 3-21G(d). The structure of nitrobenzene derivatives in this calculation is shown in Figure 2.



Nitrobenzene (NB)

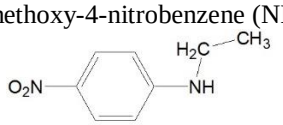


1-(4-nitrophenyl)hydrazine (NB1)



4-nitrobenzamine (NB2)

1-methoxy-4-nitrobenzene (NB3)



N-ethyl-4-nitrobenzene (NB4)

Figure 2. Nitrobenzene and its derivatives structure

RESULTS AND DISCUSSION

The calculation result discussed in this article are optimized geometry, parameter geometry, atomic charge distribution, HOMO-LUMO distribution, and Infrared spectrum between nitrobenzene and its derivatives. The explanation based on the result and discussion in this study is as follows:

Nitrobenzene and Its Derivatives Optimized Structure

Nitrobenzene and its derivatives optimized structure was gained from geometry optimization calculation. The purpose of geometry optimization is to get a structure with a minimum energy of nitrobenzene and its derivatives. The nitrobenzene and its derivatives optimized structure is in one plane. One plane means planar. Planar structure has dihedral angle of about zero degrees (0^o) (Maahury & Martoprawiro, 2019). The planar structure is caused by the ring of benzene which is the main structure of nitrobenzene. Benzene in nitrobenzene has six atom carbon connected by turns double bond. The optimized geometry of nitrobenzene derivatives is shown in Figure 3.

Structure Parameter of Nitrobenzene and Its Derivatives

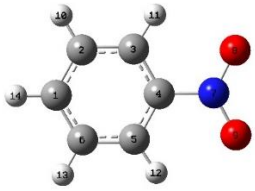
Three structure parameter terms are bond length, angle, and dihedral. Three structural parameters changed when our structure was processed for geometry optimization calculation. The change was happening until obtaining the lowest energy. The bond length, angle, and dihedral for these five molecules give the different numbers for the same backbone. It means that the presence of functional groups affects the structure parameters. The structure parameter of nitrobenzene derivatives can be seen in Table 1.

Based on Table 1, bond length C_{1-2} and C_{1-6} for derivatives are longer than nitrobenzene. Bond angle for derivatives are smaller angle than nitrobenzene. The reduced angle indicates the repulsion between the atoms with the different functional groups

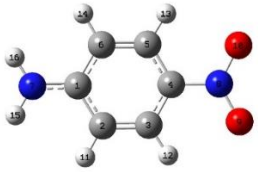
Atomic charge Distribution of Nitrobenzene and Its Derivatives

Besides discussion about the structure after optimization, the other important information to the discussion is the atomic charge. Knowing how the functional group affects the molecule's atomic charge distribution is necessary. The charge distribution explains the changing of charge in backbone when it bonded to different functional group. Atomic charge

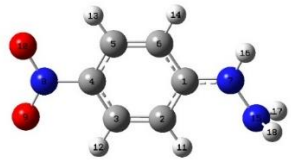
distribution around the backbone structure (benzene) is shown in Table 2. Based on data in Table 1, there are the different atomic charge distributions for nitrobenzene and its derivatives. The clear difference that can be seen is that the C1 charge in nitrobenzene has a negative number, while its derivatives have positive numbers. The other difference is that the C4 charge in nitrobenzene has a negative number, while its derivatives have negative numbers. This result can be caused by differences in the functional groups attached to the C1 atom and causes the distribution of atomic charge distribution to the C4. in Nitrobenzene, C1 is only bonded to a hydrogen atom. At the same time, its derivatives are bound to various functional groups.



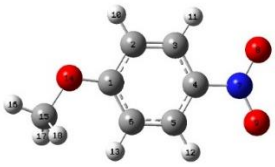
(a)



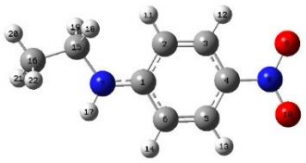
(b)



(c)



(d)



(e)

Figure 3. Nitrobenzene Derivatives Optimized Structure (a) NB, (b) NB1, (c) NB2, (d) NB3 (e) NB4

HOMO-LUMO Distribution of Nitrobenzene and its Derivatives

The HOMO and LUMO show how the distribution of molecular orbitals for the molecule. HOMO-LUMO distribution can also show how an electron can easily be transferred. The overlap between HOMO and LUMO allows electrons to be excited easily (Maahury et al., 2019). HOMO-LUMO distribution of nitrobenzene and its derivatives are shown in Figure 4.

The Distribution of HOMO-LUMO shows a difference between HOMO and LUMO in Nitrobenzene and its four molecule derivatives. The HOMO of Nitrobenzene is only spread around the NO_2 functional group. While the HOMO of its derivatives spread throughout the molecule. LUMO of Nitrobenzene and its derivatives have the same distribution throughout the molecule but only differ in color distribution

Table 1. Structure Parameter of Nitrobenzene Derivatives

Molec-ule	Bond length (Å)		Bond angle (°)		Dihedral (°)
	r_{1-2}	r_{1-6}	a_{1-2-6}	a_{3-4-5}	$d_{1-2-3-4}$
NB	1.3985	1.3995	120.292	121.9794	0.00
NB1	1.4124	1.4154	118.584	120.1667	0.00
NB2	1.4168	1.4172	117.9912	120.4117	0.0
NB3	1.4081	1.4031	119.5285	121.0208	0.0
NB4	1.4179	1.4211	117.8236	120.3447	0.0

Table 2. Atomic charge distribution of nitrobenzene derivatives

Molecule	Atomic charge					
	C1	C2	C3	C4	C5	C6
NB	-0.168611	-0.187712	-0.173338	0.299667	-0.173400	-0.187715
NB1	0.725499	-0.198390	0.299464	-0.437939	0.286016	-0.259129
NB2	0.734273	-0.239243	0.296337	-0.433888	0.295908	-0.238669
NB3	0.719402	-0.171323	0.227313	-0.314218	0.242897	-0.208716
NB4	0.774191	-0.267382	0.331640	-0.481279	0.303833	-0.278640

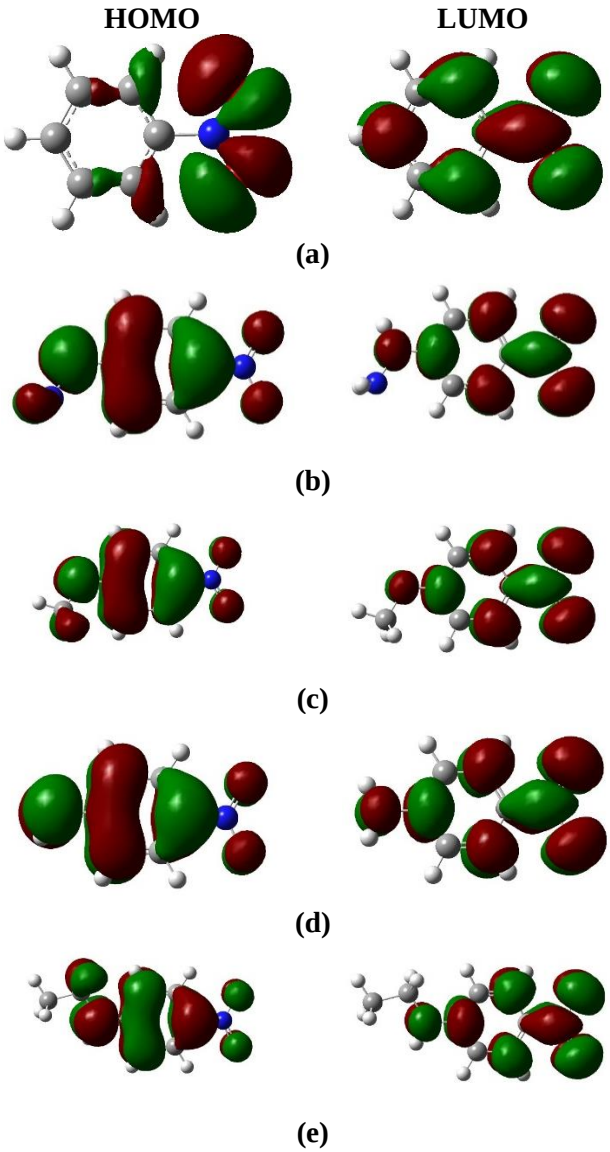


Figure 4. HOMO Distribution (a) and LUMO distribution (a) NB, (b) NB1, (c) NB2, (d) NB3 (e) NB4

Infrared Spectrum of Nitrobenzene Derivatives

The calculation of the vibration frequency is carried out to see the relationship between IR absorption and its intensity. Each type of bond will have a different frequency, so it can be used to determine the type of bond, structure, or functional group. The infrared spectrum shows the fingerprints for each molecule in the calculation (Maahury, et al., 2020). It shows the functional group of calculated molecules. The infrared spectrum of nitrobenzene derivatives is shown in Figure 4.

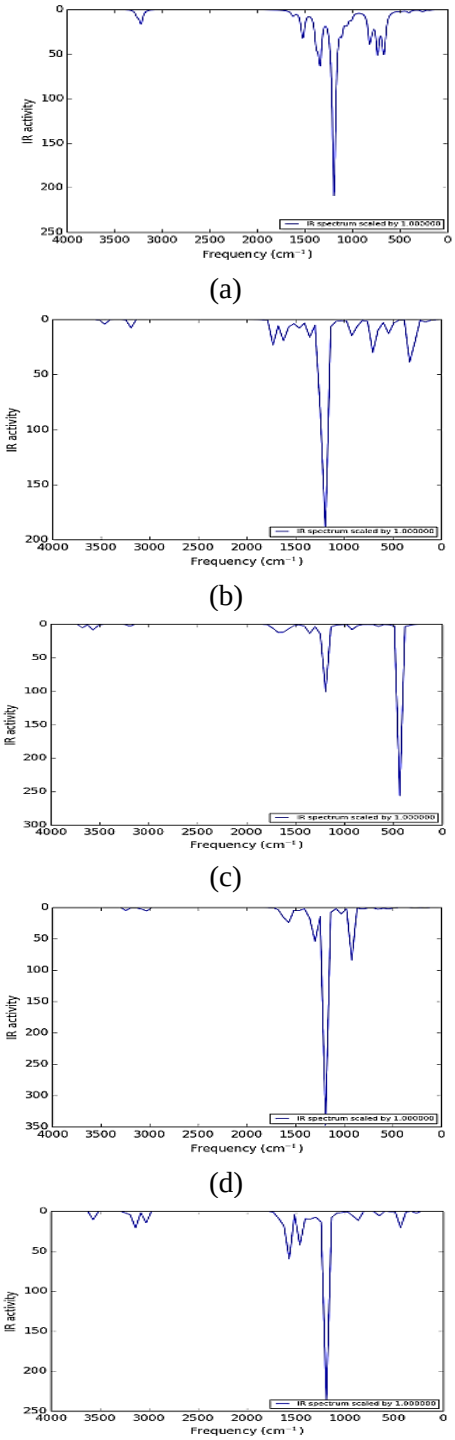


Figure 5. Infrared spectrum (a) NB, (b) NB1, (c) NB2, (d) NB3 (e) NB4

CONCLUSION

Computational calculations for nitrobenzene and its four nitrobenzene derivatives have been successfully done. The optimized structure is in one plane or planar.

There are changing parameter structures, increasing bond length, and decreasing bond angle when the substituent is present in derivatives. The electronic properties show the same distribution of atomic charge and HOMO-LUMO.

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