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Research Article

Theoretical study to determine the band gap of the bis(benzoylacetone)zirconium complex compound using the PM3 semi-empirical computational method

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Keywords

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Abstract

The bis(benzoylacetone)zirconium (bis(bzac)2Zr) complex compound has been used as a catalyst in various chemical reactions. The aim of this study was to compare the band gap and maximum wavelength of the bis(bzac)2Zr complex with its ligands. The software used is HyperChem 8.0. Calculations begin by optimizing complex compounds. After that, the HOMO-LUMO energy is calculated so that the band gap is obtained. Meanwhile, the calculation of the maximum wavelength is carried out based on UV calculations by using the singly excited method. The addition of Zr atoms to the ligand is expected to reduce the band gap of the complex. On the other hand, the maximum wavelength of the resulting complex is expected to be higher than that of the ligand. Based on the calculation results, the band gap of the complex compounds is 6.128 eV, while the maximum wavelength produced is 383.54 nm. The band gap of the ligand is larger than that of the complex, which is 9.031 eV, while the maximum wavelength of the ligand is 261.25 nm.

Introduction

Computational chemistry has grown rapidly since the end of the decade because it can be used to simulate chemical reaction mechanisms. In addition, computational chemistry can also determine the chemical and physical properties of a molecule. In computational chemistry, calculations are performed using certain algorithms with models that have been designed by theoretical experts. With this method, the computational calculations performed can produce a picture of results that are almost similar to experimental results (Prianto, 2007).

In previous studies, we have reported on computational studies regarding the proposed reaction mechanism. These calculations are carried out to provide an overview of reaction conditions to researchers when conducting experiments in the laboratory. The reaction mechanism that we have calculated is regarding the acetalization of benzaldehyde to produce benzaldehyde dimethyl acetal and the oligomerization of glycerol to produce glycerol oligomer (Yusuf 2017, 2020; Yusuf and Nasution, 2022).

Previously, several researchers had also conducted computational studies to determine the physical and chemical properties of a molecule, including the band gap and maximum wavelength of some organic and inorganic molecules. These molecules include ZrCl4 (Nevarez et al. 2019), Be-Porphyrin, Co and Be-Phthalocyanine (Khairani and Siregar, 2015; Siregar and Sinaga, 2017; Siregar and S, 2019), 8-hydroxyquinoline, and porphyrin conjugated with Ca metal atoms. On the other hand, they also observed the effect of adding metals on changes in the band gap of the molecule. The addition of the Fe central atom to the 8-hydroxyquinoline ligand has reduced the band gap of the complex. As a result, the process of excitation of electrons from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). Meanwhile, the maximum wavelength of the resulting complex is also longer than that of the ligand

(Pamungkas and Sanjaya, 2013; Saputra and Sanjaya, 2014). Based on this, it is expected that the addition of Zr atoms to bzac ligands will also reduce the band gap and increase the maximum wavelength.

Besides the addition of Fe atoms, the researchers also observed the addition of Be, Co, and Ca atoms. As a result of a decrease in the band gap after the addition of metal elements, the resulting complex compounds can be utilized as semiconductor materials and sensors that have photosensitivity properties with high sensitivity (Male et al. 2015; Khairani and Siregar, 2015; Siregar and Sinaga, 2017; Siregar and S, 2019). Based on the band gap theory, a material can be categorized as a semiconductor material, if the band gap is between 0.18 eV to 3 eV (Ismangil et al. 2021).

In this research, a computational study was carried out to determine the band gap and maximum wavelength of the bis(bzac)2Zr complex. As a comparison, the band gap and maximum wavelength of the bzac ligand are also calculated. The bis(bzac)2Zr complex was previously used as an acid catalyst in a variety of chemical reactions, including the ring opening of δ-valerolactone, ε-caprolactone, and oxirane. The resulting polylactone can be used as a biomedical material, such as for tissue repair, implants, surgical sutures, and biodegradable packaging (Yusuf et al. 2022).

Method

Materials

The computational method used is semi-empirical PM3. While the materials calculated are bis(bzac)2Zr complex compounds and bzac ligands. The bis(bzac)2Zr complex 2D molecular structure are depicted in Fig.-1.

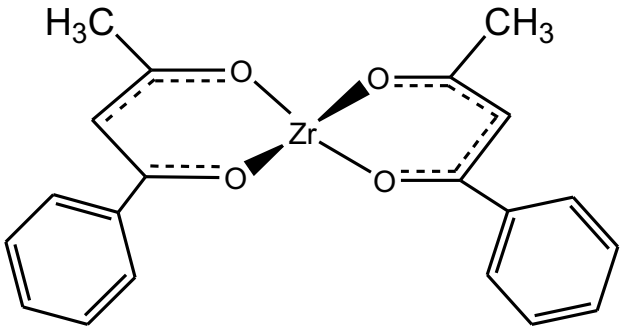

Fig.-1. The bis(bzac)2Zr Complex 2D Molecular Structure

Equipment

Computation calculations are performed using the Windows operating system version 10. Meanwhile, the Hyperchem 8.0.2 software is used to calculate geometry optimization, band gap, wavelength, and molecule visualization (Yusuf et al. 2023).

Geometry Optimization

The HyperChem software is used to calculate bis(bzac)2Zr complexes and bzac ligands. Molecules are drawn in 2D and then converted to 3D. The initial optimization process is carried out using the invoke model builder. The next optimization process is carried out using the PM3 semi-empirical method to obtain the most stable state with minimal energy (Yusuf and Nasution, 2022).

Band Gap

Determination of the band gap is done through the compute menu and orbitals. After that, standardization of HOMO and LUMO is carried out under the same conditions at 0. The next stage is selecting labels and plots. Next, the calculation of the band gap is carried out based on the difference in energy in the LUMO and HOMO states (Siregar and Sinaga, 2017).

Electronic Transition Spectra Analysis (UV)

Prior to UV calculations, it is necessary to confirm the geometric optimization of the complexes and ligands. After that, UV calculations are carried out by selecting the compute, single point, and single point CI menus. Meanwhile, the method used is singly excited. Based on the UV data, the maximum wavelength of the complexes and ligands is obtained.

Results and Discussion

In order to obtain the most stable molecular structure with a minimum energy level, geometry optimization is carried out on complex compounds and ligands (Siregar and Sinaga, 2017; Siregar and S, 2019). In complex compounds, there are two bzac ligands coordinated to one Zr central atom. The geometry of the optimization results is shown in Fig.- 2 and Fig.-3.

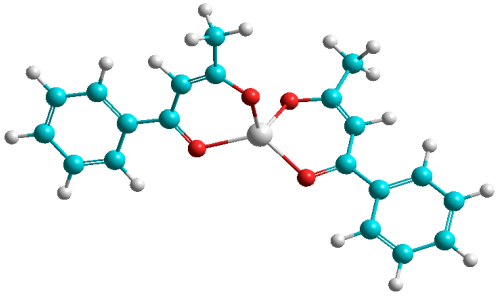

Fig.-2. Optimized Bis(bzac)2Zr Complex

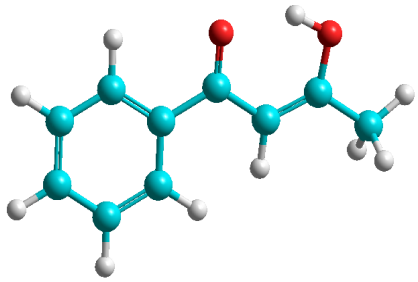

Fig.-3. Optimized Bzac Ligand

Band Gap

The LUMO and HOMO energies of the bzac ligands obtained through computational calculations are shown in Fig.- 4 and Fig.-5.

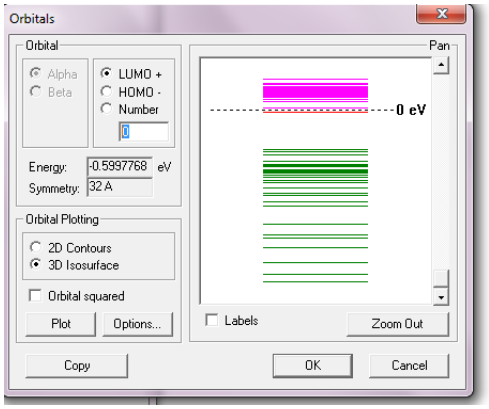

Fig.-4. The LUMO Energies of the Bzac Ligands

The band gap is calculated based on the difference between the LUMO energy and the HOMO energy, as shown in Table 1. The HOMO energy of the bzac ligand is -9.631417 eV, while the LUMO energy is -0.5997768 eV. The band gap of the bzac ligand was obtained at 9.031 eV. The high band gap of the ligand causes it to have low conductivity because it requires high energy to carry out the electron excitation process from HOMO to LUMO (Khairani and Siregar, 2015). Furthermore, Fig.-6 and Fig.-7 also depicts the LUMO and HOMO energies of the bis(bzac)2Zr complex derived from computational calculations.

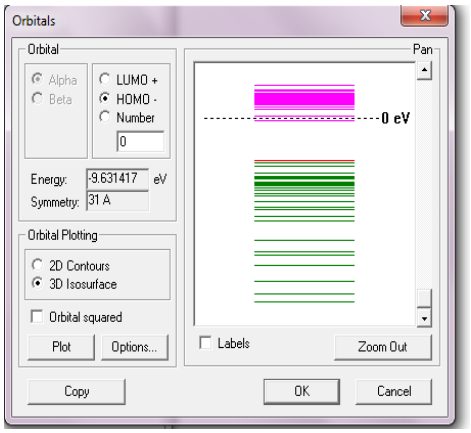

Fig.-5. The HOMO Energies of the Bzac Ligands

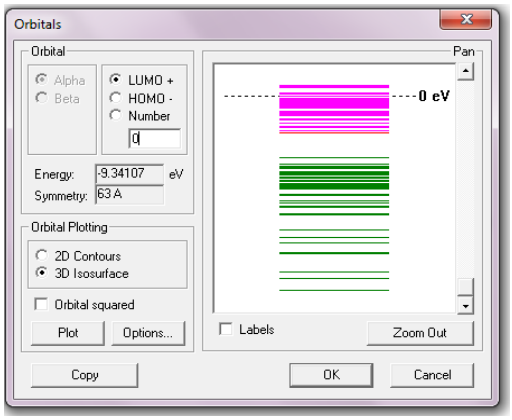

Fig.-6. The LUMO Energies of the bis(bzac)2Zr Complex

The LUMO energy in the bis(bzac)2Zr complex is -9.34107 eV and the HOMO energy is -15.46933 eV. Meanwhile, the band gap of the complex is 6.128 eV as shown in Table 2. The presence of a Zr central atom in the bis(bzac)2Zr complex narrows the band gap compared to the ligand. This happens because the Zr atom has a small ionization energy, so it can easily release electrons when coordinating with a ligand. As a result, the conductivity of the complex is greater than that of the bzac ligand. Previously, the addition of metals to an organic molecule has also been carried out by previous researchers to produce a narrower band gap (Indriani et al., 2018; Siregar and S, 2019).

Table 1. Bzac Ligand Band Gap

Ligand	Homo. E (eV)	Lumo. E (eV)	Band gap (eV)
Bzac	-9.631417	-0.5997768	9.031

Table 2. The Band Gap of the Bis(bzac)2Zr Complex

Complex	Homo. E (eV)	Lumo. E (eV)	Band gap (eV)
$Bis(bzac)_2Zr$	-15.46933	-9.34107	6.128

A narrower band gap will cause the distance between the conduction band and the valence band to be closer (Indriani et al. 2018). As a result, the process of excitation of electrons from HOMO to LUMO becomes easier because the energy required becomes smaller. Compounds with a narrower band gap (0.18 eV to 3 eV) will have good conductivity and photosensitivity properties so that they can be applied as semiconductor, optical and optoelectrical materials (Male et al. 2015; Siregar & S, 2019; Ismangil et al. 2021). Whereas, compounds that have a wide band gap above 3 eV will have insulating properties.

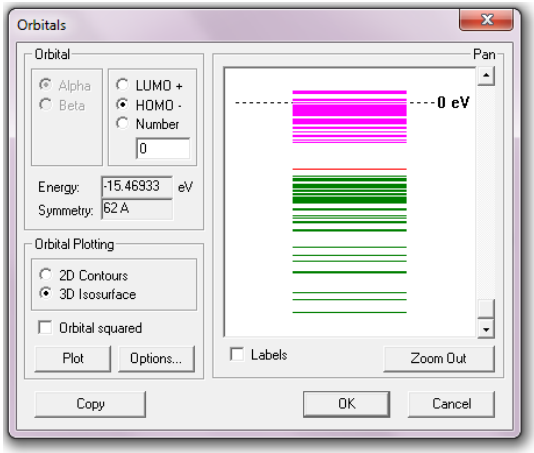

Fig.-7. The HOMO Energies of the Bis(bzac)2Zr Complex

Table 1. Maximum Wavelength Of Bzac Ligand and Bis(bzac)$_2$Zr Complex

Compound	Maximum wavelength λ max (nm)
Bzac	261.25
Bis(bzac)$_2$Zr	383.54

In the previous research report by the Nevarez group, band gap measurements were carried out in molecules that have a Zr central atom. This compound is the result of ZrCl4 product fragmentation, which was analyzed using mass spectrometry. The molecules measured included ZrCl (0.46 eV), ZrCl2 (3.84 eV), ZrCl3 (3.53 eV), and ZrCl4 (4.35 eV). Of the four molecules, the ZrCl molecule can be a semiconductor. While the other three molecules are insulators because they have a band gap above 3 eV (Nevarez et al. 2019).

UV Spectra of the Bis(bzac)2Zr Complex Compound

The UV spectra of the bis(bzac)2Zr complex and its ligands are shown in Fig.-8 and Fig.-9. Molecules with narrow band gaps will absorb longer maximum wavelengths. Meanwhile, molecules that have a wider band gap will absorb shorter maximum wavelengths (Saputra and Sanjaya, 2014). As a result, molecules with narrow band gaps will have better photosensitivity properties.

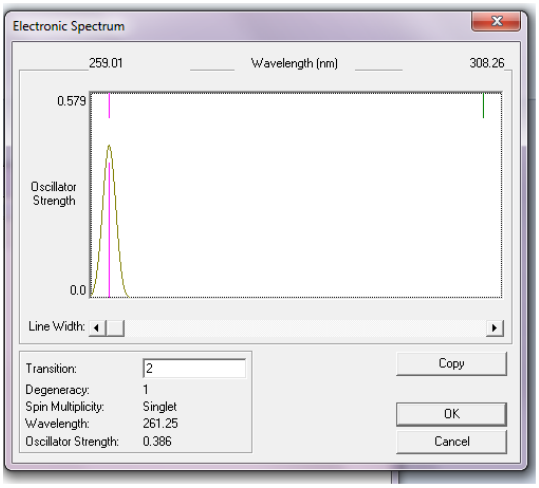

Fig.-8. UV Spectra of the Bis(bzac)2 Ligand

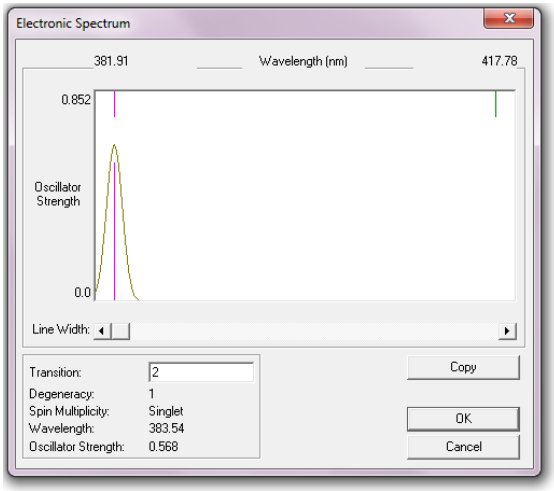

Fig.-9. UV Spectra of the Bis(bzac)2Zr Complex

According to the calculation results, the bis(bzac)2Zr complex has a longer wavelength than the ligand, as shown in Table 3 and Fig.-9. This is because the complex has a narrower band gap than the ligand. The addition of the Zr central atom to the complex causes the maximum wavelength to increase to 383.54 nm, while the ligand only has a maximum wavelength of 261.25 nm (Fig.-8).

Conclusion

Based on the calculations, the band gap of the complex compound bis(bzac)2Zr was found to be 6.128 eV. Meanwhile, the band gap of the ligands is wider than that of complex compounds, which is equal to 9.031 eV. Furthermore, the maximum wavelength of the complex is higher than that of the ligand, which is equal to 383.54 nm. Whereas, the maximum wavelength of the ligand is 261.25 nm. The narrow band gap of complexes is due to the addition of zirconium atoms, which can reduce the band gap of complex compounds. Complex compounds that require less energy to excite from HOMO to LUMO will absorb light at longer wavelengths. Conversely, ligand molecules that require a lot of energy to excite will absorb light at shorter wavelengths.

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Conflict of Interests

The author (s) declares that there is no conflict of interest in this research and manuscript.

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