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# An ab initio study of the reaction mechanism of 2-methylbenzaldehyde acetalization with methanol

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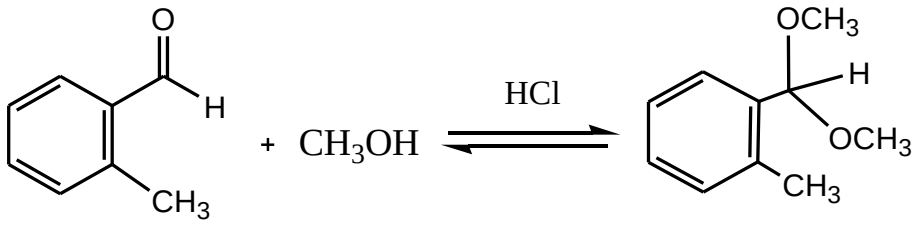
ABSTRACT

Acetalization of 2-methylbenzaldehyde is a type of reaction that occur by reacting 2-methylbenzaldehyde with methanol. Meanwhile, the catalyst used in the reaction is an acid catalyst. This research was conducted to determine the pathway of the intermediate reaction mechanism that is most likely to produce 2-methylbenzaldehyde acetal product. The software used in this research is HyperChem 8.0, 6-31G* basis sets, with the ab initio method. Before being calculated, the molecular structure is drawn with a 2-dimensional view. After that, the molecular structure is converted into a 3D view and geometry optimization is carried out. The results obtained are in the form of optimized energy from the structure of reactant 2-methylbenzaldehyde, several intermediate products, and product 2-methylbenzaldehyde acetal.

## 1. Introduction

Acetalization is one of the most frequently used reaction models to protect aldehydes. The resulting acetal is often used as a solvent and as an intermediate in the synthesis of organic, inorganic, and pharmaceutical compounds (Arrozi et al. 2015; Han et al. 2014; Smirnov et al. 2018; Yi et al. 2017; Yu et al. 2020). As shown in Figure 1, acetalization reactions are usually carried out by reacting the carbonyl group with an alcohol using an acid compound as a catalyst (Arrozi et al. 2015).




2-methylbenzaldehyde 2-methylbenzaldehyde acetal

Figure 1. Acetalization reaction of 2-methylbenzaldehyde

In order to obtain acetal product compounds, it is necessary to perform simulations through computational calculations. The simulation will provide an overview of the most likely reaction routes in the formation of acetals. As a result, the structures of the reactants, intermediates, and products will be obtained which are similar to the experimental results. This step is taken to minimize the failure rate, time, and cost of research

when conducting experiments in the laboratory. During the simulation, the ab initio method will be used with certain basis sets in order to get a stable molecular structure with the least amount of energy (Dutta Pal et al. 2017; Rocha et al. 2015; Santos & Ribeiro Da Silva, 2014; Wang et al. 2021; Yang & Zhang, 2015). Previously, computational calculations using the ab initio method on the synthesis of nitro-eugenol compounds have also been carried out. As a result, there is a good correlation between computational calculations with experiments so that the number of failures and costs of experiments can be kept to a minimum (Septiana, 2018).

The Ab initio method can be solved using the Schrödinger equation by separating the motion of the nucleus and electrons. The approach used is the Born-Oppenheimer equation, which assumes that the motion of the nucleus will be slower than the movement of the electrons. The next step is to solve the wave function of the molecule. The high accuracy of the ab initio method makes it difficult to calculate the structure of large molecules. However, this method can be used to calculate the structure of small molecules so that a more accurate stable state is obtained (Pranowo, 2000).

Previously, our research group has carried out computational calculations of benzaldehyde compounds to produce acetal products such as benzaldehyde (Yusuf & Sitepu. 2017), 2-hydroxybenzaldehyde (Yusuf et al. 2017), 2-methoxybenzaldehyde (Yusuf et al. 2019), 2-chlorobenzaldehyde (Yusuf. 2020), and 3-chlorobenzaldehyde (Yusuf, 2019). The results we have obtained are the most likely reaction routes in the benzaldehyde acetalization reaction. The resulting product also has less energy than the intermediate compound. In this study, computational calculations will also be carried out to obtain the most likely reaction route to produce a 2-methylbenzaldehyde acetal product with 2-methylbenzaldehyde as a substrate.

## 2. Method

### *2.1. Materials*

The method used is ab initio, and the material is the structure of the compound 2-methylbenzaldehyde, the intermediate, and the product 2-methylbenzaldehyde acetal.

### *2.2. Equipment*

All molecular geometry optimization calculations were performed using the HyperChem 8.0 software with the ab initio method at the HF level and using the 6-31G* basis sets. The algorithm used is the Polak-Ribiere RMS conjugate gradient with a gradient of 0.01 kcal/Åmol and the maximum number of cycles is 32767 scans. While the computer equipment used has the following specifications: Intel (R) core (TM) i3-6100T, system type 64-bit OS, 3.20 GHz CPU, and 4.00 GB of RAM (Yusuf, 2020).

### *2.3. 2.3 Computational Calculation*

The molecular sample to be counted is drawn in a 2D view and then converted into a 3D view. After that, sample settings were carried out which included charge, spin multiplicity, RHF spin pairing and the ab initio method. The computational calculation begins with a start log and will be completed when the calculated molecule has been optimized. If the energy, distance, and angle of the results are abnormal, the procedure will be repeated again from the beginning until the molecular structure has been optimized (Pranowo, 2000).

## 3. Results and Discussion

### *3.1. The 2D View of the Molecular Structure*

Molecular modeling of the benzaldehyde acetalization reaction was carried out to determine the behavior of the molecule to be calculated. The 2D view of the molecular structure of reactants, intermediate compounds, and products is shown in Figure 2.

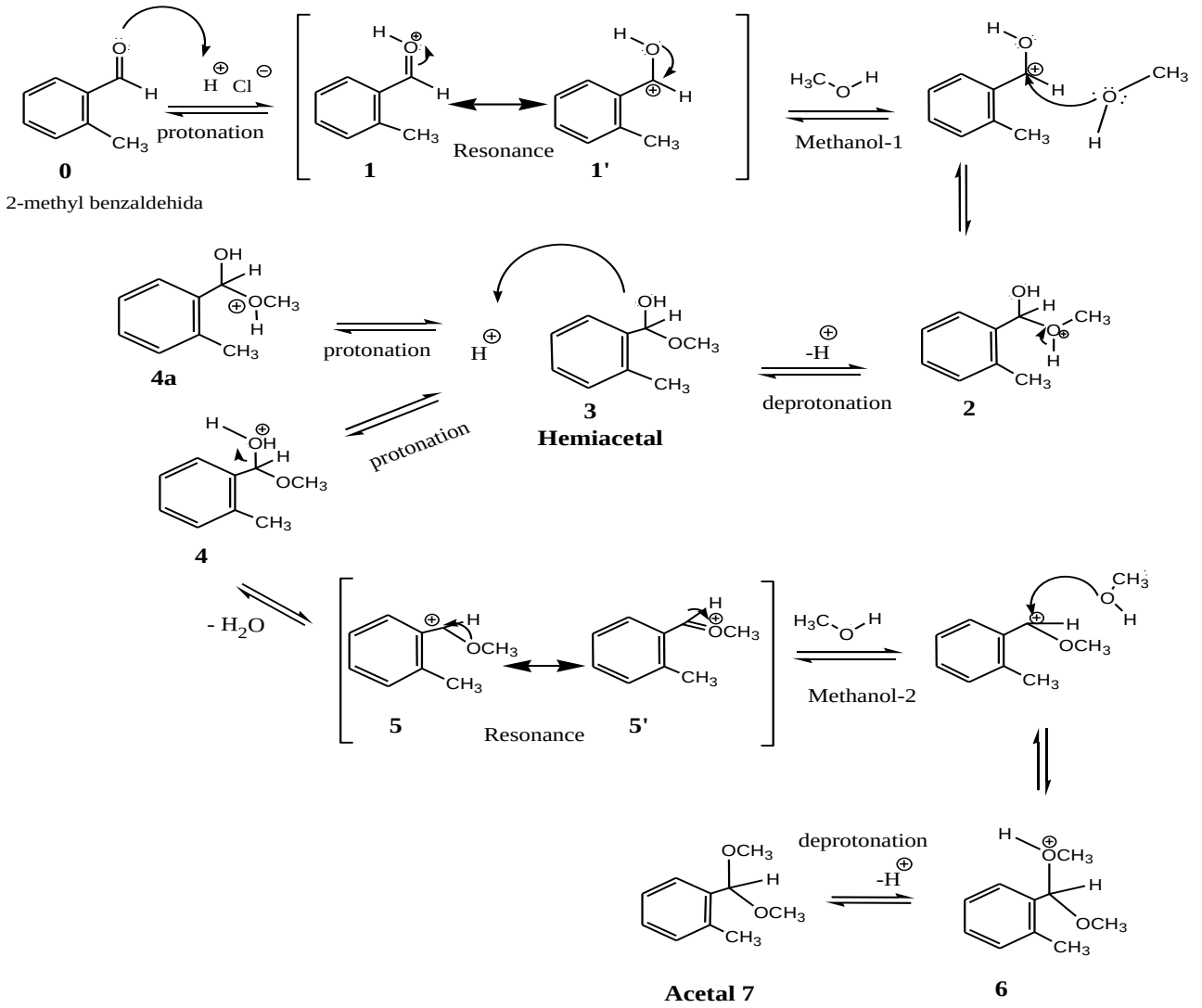



Figure 2. The Proposed Reaction Mechanism for the Formation of 2-Methylbenzaldehyde Acetal.

The mechanism for the formation of 2-methylbenzaldehyde acetal based on Figure 2 starts from the protonation of 2-methylbenzaldehyde to form compound 1. Compound 1 can resonate to form compound 1'. After that, the O atom of methanol will attack the C atom to form compound 2. Then, deprotonation occurs and a hemiacetal is formed. Protonation occurs again and forms compound 4. Alternatively, compound 4a is also calculated to determine a more stable molecular structure. Furthermore, the leaving group H2O will be separated from compound 4 and form compound 5. Compound 5 can resonate to form compound 5'. After that, the O atom from methanol will attack the C atom again to form compound 6. In the final stage, deprotonation occurs again and product 7 is formed (Dong et al. 2018).

### *3.2. Geometry Optimization*

In this study, geometric optimization was carried out to calculate the lowest energy and the smallest interatomic force of the sample molecule. The result obtained is that the structure is the most stable and close to the real structure in nature (Pranowo, 2000). A molecular structure will be stable if there are repulsive and attractive forces in a state of equilibrium. As a result, interaction energy and potential energy will be at their lowest levels. Whereas, If a molecular structure has a large potential energy, it will require a greater dissociation energy to change the molecule into a stable state. The molecular structure of the optimization results obtained in this study is shown in Figure 3.

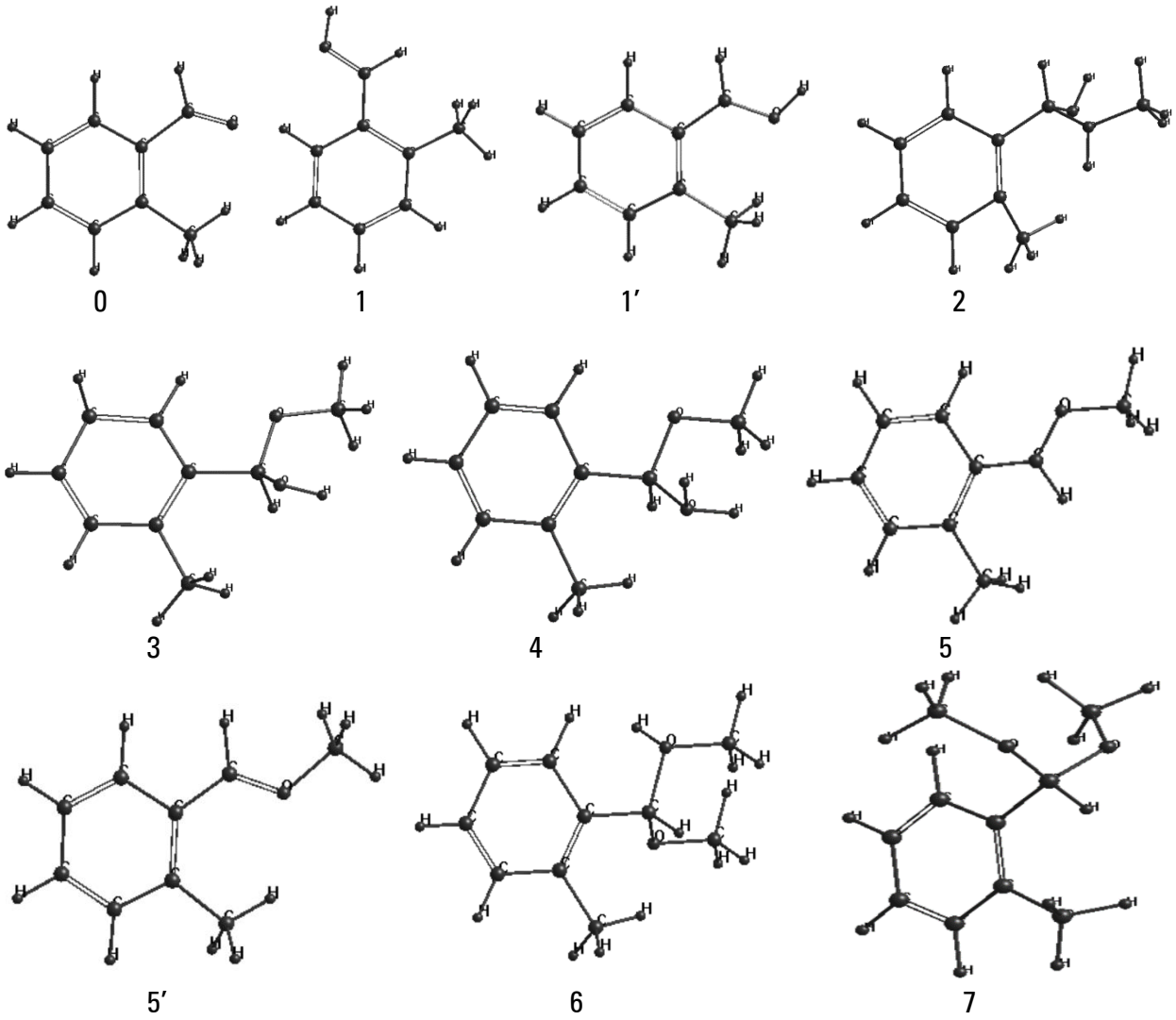



Figure 3. Geometric Optimization Results of Reactant, Intermediate Compounds, and Product

### *3.3. Total Energy*

In addition to displaying optimized molecular structure images, the calculation results also display data in the form of log files containing the minimum energy of a molecule. The calculation of the total minimum potential energy of the molecular structure (ΔE) is in accordance with equation 1.

$$\Delta E_{total} = E_{product} - E_{reactant}$$

Eproducts reflect the total energy of the products, while Ereactant reflect the total energy of the reactants. The results of the calculation of the minimum energy for each reaction step, including reactants (0), intermediates (1–6), and products (7), are shown in Figure 4.

The molecular structure of the reactant 0 is the most stable structure among other structures. This phenomenon is caused because the reactant molecules have the least energy based on the calculation results as shown in Figure 4. Meanwhile, the product structure 7 has a lower energy than the intermediate compounds 1-6. These results indicate that the molecular structure of the product has more balanced repulsive and attractive forces than the intermediate compound. As a result, the interaction energy and potential energy needed to form the product into a stable condition will be at a minimum when compared to intermediate compounds 1-6 (Yusuf et al. 2019).

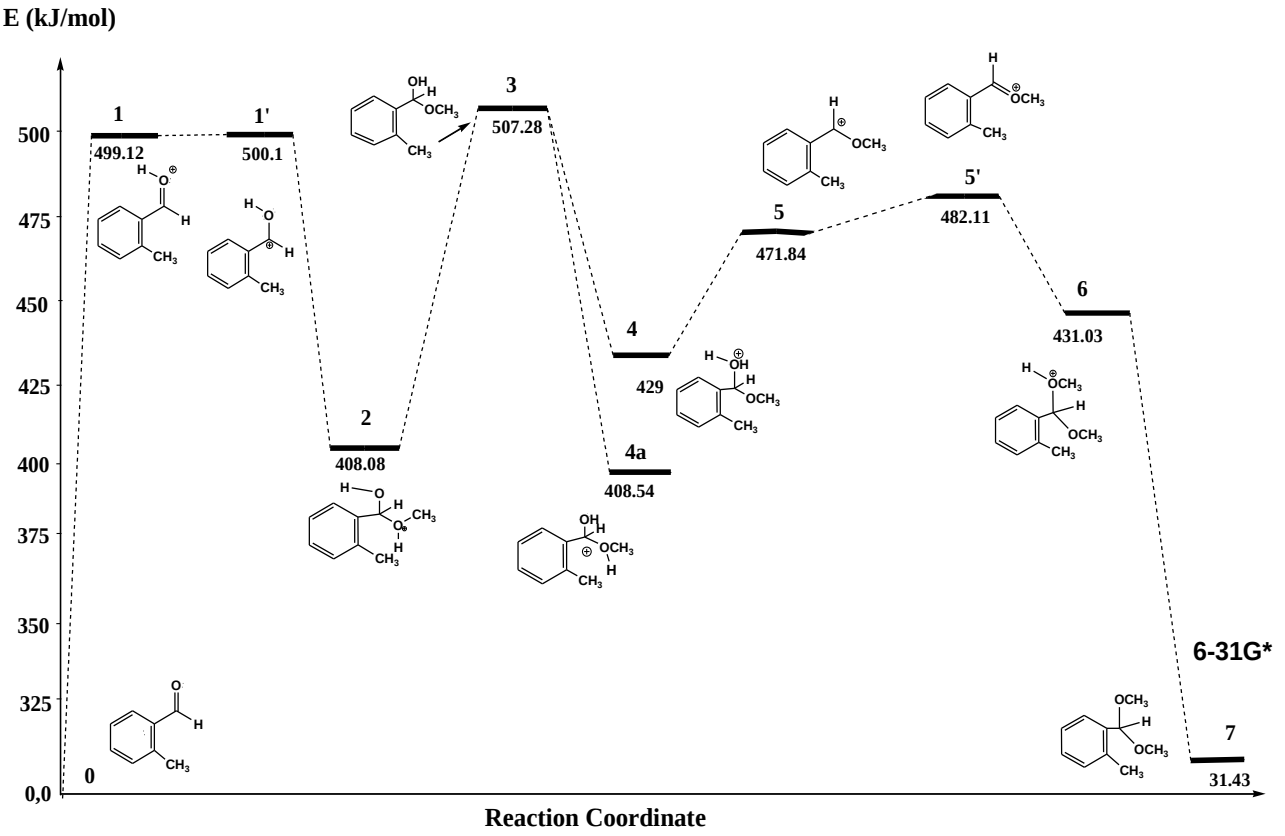



Figure 4. Acetalization Reaction Energy Profile of 2-Methylbenzaldehyde.

## 4. Conclusion

Computational calculations using the ab initio method have been successfully carried out. As a result, the most likely reaction route to produce the 2-methylbenzaldehyde acetal product was obtained. The reaction mechanism steps start from protonation of 2-methylbenzaldehyde by an acid catalyst, formation of hemiacetal, and formation of a 2-methylbenzaldehyde acetal product. The molecular structure of the product has a more stable state than hemiacetal and other intermediate compounds. These results indicate that the 2-methylbenzaldehyde acetal product has a lower interaction energy and potential energy than hemiacetal compound and other intermediate compounds.

## References

Arrozi, U. S. F., Wijaya, H. W., Patah, A., & Permana, Y. (2015). Efficient acetalization of benzaldehydes using UiO-66 and UiO-67: Substrates accessibility or Lewis acidity of zirconium. *Applied Catalysis A: General*, 506, 77–84. https://doi.org/10.1016/j.apcata.2015.08.028

Dong, J. L., Yu, L. S. H., & Xie, J. W. (2018). A Simple and versatile method for the formation of acetals/ketals using trace conventional acids. *ACS Omega*, 3(5), 4974–4985. https://doi.org/10.1021/acsomega.8b00159

Dutta Pal, G., Dutta, B., Ganguly, T., & Chowdhury, J. (2017). Role of gold nanocolloids on the photostability of 2-hydroxy-5-methyl benzaldehyde molecule and evidence of excited state intramolecular proton transfer process aided by DFT, non-adiabatic Ab Initio molecular dynamics simulations. *Journal of Luminescence*, 188, 378–387. https://doi.org/https://doi.org/10.1016/j.jlumin.2017.04.038

Han, X., Yan, W., Chen, K., Hung, C. Te, Liu, L. L., Wu, P. H., Huang, S. J., & Liu, S. Bin. (2014). Heteropolyacid-based ionic liquids as effective catalysts for the synthesis of benzaldehyde glycol acetal. *Applied Catalysis A: General*, 485, 149–156. https://doi.org/10.1016/j.apcata.2014.08.001

Pranowo, H. D. (2000). Kimia Komputasi. Universitas Gadjah Mada Press.

Rocha, M., Di Santo, A., Arias, J. M., Gil, D. M., & Altabef, A. Ben. (2015). Ab-initio and DFT calculations on molecular structure, NBO, HOMO–LUMO study and a new vibrational analysis of 4-(Dimethylamino) Benzaldehyde. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 136, 635–643. https://doi.org/https://doi.org/10.1016/j.saa.2014.09.077

Santos, A. F. L. O. M., & Ribeiro Da Silva, M. A. V. (2014). Experimental and high level ab initio enthalpies of formation of di- tri- tetra- and pentamethyl- substituted pyrroles. *Journal of Chemical Thermodynamics*, 75, 1–7. https://doi.org/10.1016/j.jct.2014.04.003

Septiana, B. N. (2018). Studi Komputasi Ab Initio Dan Sintesis Senyawa Nitroeugenol [Universitas Mataram.]. In Thesis. http://eprints.unram.ac.id/4348/

Smirnov, A. A., Selishcheva, S. A., & Yakovlev, V. A. (2018). Acetalization catalysts for synthesis of valuable oxygenated fuel additives from glycerol. *Catalysts*, 8(12), 1–25. https://doi.org/10.3390/catal8120595

Wang, H., Wang, J., Chen, J., Herbers, S., Zheng, H., & Gou, Q. (2021). Competitive and cooperative n $\rightarrow$ $\pi^*$ and n $\rightarrow$ $\sigma^*$ interactions in benzaldehyde–formaldehyde: rotational characterization. *Physical Chemistry Chemical Physics*, 23(14), 8778–8783. https://doi.org/10.1039/D0CP06409B

Yang, Y., & Zhang, P. (2015). Hydriding and dehydriding energies of PuHx from ab initio calculations. *Physics Letters, Section A: General, Atomic and Solid State Physics*, 379(28–29), 1649–1653. https://doi.org/10.1016/j.physleta.2015.04.038

Yi, H., Niu, L., Wang, S., Liu, T., Singh, A. K., & Lei, A. (2017). Visible-light-induced acetalization of aldehydes with alcohols. *Organic Letters*, 19(1), 122–125. https://doi.org/10.1021/acs.orglett.6b03403

Yu, L., Lin, C., Liao, C., Zeng, X., Chen, X., Zhu, Z., Huang, Y., Li, Y., & Chen, L. (2020). Green chemistry: efficient acetalization of aldehydes with alcohols using the acid red 52 photocatalyst. *Environmental Chemistry Letters*, 18(4), 1353–1359. https://doi.org/10.1007/s10311-020-00994-y

Yusuf, M. (2019). Theoretical Study on the Reaction Mechanism of Acetalization of 3-Chlorobenzaldehyde Catalyzed by Halogen Acid. *EAI Confrence Proceedings*, 477–484. https://doi.org/10.4108/eai.18-10-2018.2287347

Yusuf, M. (2020). Computational calculation of acetalization of 2-chlorobenzaldehyde reaction mechanism using hydrochloric acid catalyst with ab initio method. *Jurnal Pendidikan Kimia*, 12(1), 1–9. https://doi.org/10.24114/jpkim.v12i1.17707

Yusuf, M., Dahniar, D. R., & Damanik, M. (2019). Ab initio method on the mechanism of acetalization of 2-methoxybenzaldehyde using halogen acid catalysts. *Asian Journal of Chemistry*, 31(5), 982–986. https://doi.org/10.14233/ajchem.2019.21662

Yusuf, M., Roza, D., & Nasution, A. K. (2017). Acetalization of 2-Hydroxybenzaldehyde mechanism using halogen acid catalysts based on ab initio methods. *AIP Conference Proceedings*, 1904, 020055–1. https://doi.org/10.1063/1.5011869

Yusuf, M., & Sitepu, D. E. B. (2017). Computational calculation of acetalization of benzaldehyde using acid catalysts (HCl) with computational method (Ab-Initio). *AIP Conference Proceedings*, 1803. https://doi.org/10.1063/1.4973182